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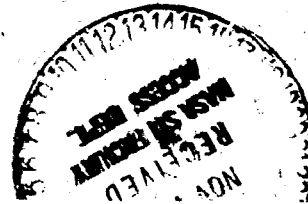
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Coal Desulfurization by Chlorinolysis Production and Combustion Test Evaluation of Product Coals

Final Report

John Kalvinskas
Dave Daly



(NASA-CR-169515) COAL DESULFURIZATION BY
CHLORINOLYSIS PRODUCTION AND COMBUSTION TEST
EVALUATION OF PRODUCT COALS Final Report
(Jet Propulsion Lab.) 71 p HC A04/HF A01

N83-13189

Unclas

CSCL 07D G3/25 01198

April 30, 1982

Prepared for
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
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Abstract

The "Coal Desulfurization by Chlorinolysis-Production and Combustion Test Evaluation of Product Coals," was conducted by the Jet Propulsion Laboratory, California Institute of Technology, under DoE Interagency Agreement No. DE-AI01-77ET12547, Mod. A007 with NASA for the period September 1, 1981 through April 30, 1982.

Laboratory-scale screening tests were carried out on PSOC 276, Pittsburgh Coal from Harrison County, Ohio to establish chlorination and hydrodesulfurization conditions for the batch reactor production of chlorinolysis and chlorinolysis-hydrodesulfurized coals. In addition, three bituminous coals, Pittsburgh #8 from Greene County, PA, Illinois #6 from Jackson County, Illinois and Eagle #5 from Moffat County, Colo. were treated on the lab scale by the chlorinolysis process to provide 39-62% desulfurization. Two bituminous coals (PSOC 276, Pittsburgh Coal from Harrison County, Ohio and 282, Illinois #6 Coal from Jefferson County, Illinois) and one subbituminous coal (PSOC 230, Rosebud Coal from Rosebud County, Montana) were then produced in 11-15 pound lots as chlorinolysis and hydrodesulfurized coals. The chlorinolysis coals had a desulfurization of 29-69%, reductions in volatiles (12-37%) and hydrogen (6-31%). Hydrodesulfurization provided a much greater desulfurization (56-86%), reductions in volatiles (77-84%) and hydrogen (56-64%).

The three coals were combustion tested in the Penn State "plane flame furnace" to determine ignition and burning characteristics. All three coals burned well to completion as: raw coals, chlorinolysis processed coals and hydrodesulfurized coals. The hydrodesulfurized coals experienced greater ignition delays and reduced burning rates than the other coals because of the reduced volatile content. It is thought that the increased open pore volume in the desulfurized-devolatilized coals compensates in part for the decreased volatiles effect on ignition and burning.

Preface

The work described in this report was performed by the Control and Energy Conversion Division of the Jet Propulsion Laboratory and the Pennsylvania State University, College of Earth and Mineral Sciences, Department of Materials Science and Engineering, Fuel Science Section, Fuels and Combustion Laboratory.

Acknowledgement

The Plane Flame Combustion Tests on JPL-Desulfurized Coal that are included in the Appendix and referred to throughout the report were performed by the Pennsylvania State University Fuels and Combustion Laboratory under subcontract (JPL Contract Number 956123) to the Jet Propulsion Laboratory, California Institute of Technology as part of the contractual effort sponsored by DoE under Interagency Agreement No. DE-AI01-77ET12547, Mod. A007 with NASA. Participants in the Pennsylvania State University combustion tests were: Dr. James J. Reuther, Assistant Professor of Fuel Science and Principal Investigator, Mr. H. T. Kim and Mr. J. G. H. Lima, Graduate Assistants in Fuel Science. The research efforts of Dr. James Reuther and his Graduate Assistants in carrying out a successful series of tests on the JPL-desulfurized coal samples are appreciated and deserve commendation.

Foreword

This is a final report for the "Coal Desulfurization by Chlorinolysis-Production and Combustion Test Evaluation of Product Coals," conducted by the Jet Propulsion Laboratory under DoE Interagency Agreement No. DE-AI01-77ET12547 with NASA for the period of September 1, 1981 through April 30, 1982. The reported work covers (1) laboratory scale and bench-scale screening tests of the chlorination and hydrodesulfurization reactions to define an optimum set of processing conditions from the perspective of maximum sulfur removal and minimum loss of coal volatiles (2) batch reactor production of approximately 15 pounds each of three desulfurized coals using the chlorinolysis process and the combination of chlorinolysis and hydrodesulfurization and (3) combustion test evaluation of the three coals, PSOC 276, (Pittsburgh Coal from Harrison County, Ohio), PSOC 282 (Illinois #6 coal from Jefferson County, Illinois) and PSOC 230 (Rosebud Coal from Rosebud County, Montana) in the raw state ground to -200 mesh, the chlorinolysis processed coals and the combination of chlorinolysis and hydrodesulfurized processed coals. (NASA Task RD-152, Amendment 187.)

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I. Introduction

JPL initiated the development of the Chlorinolysis Process for Coal Desulfurization in 1976 under the JPL Director's Discretionary Fund. The preliminary results of coal desulfurization by chlorinolysis attracted Bureau of Mines funding for a four-month laboratory screening study of twelve bituminous, subbituminous and lignite coals obtained from the eastern, midwestern and western regions of the United States (ref. 1). The follow-on work, phases II and III, (ref. 2 and 3) was funded by DoE and included substantial development and modification of the process to provide process improvements and reduced process cost. In order to obtain increased coal desulfurization above the level of 60 to 65% achieved with the chlorinolysis process, a hydrodesulfurization treatment of the chlorinated coal was introduced as part of the coal dechlorination stage. The addition of hydrodesulfurization treatment can provide up to 90% coal desulfurization which includes substantial removal of organic sulfur.

The current program is designed to investigate the combustion characteristics of desulfurized coals. Three coals, PSOC 276 (Pittsburgh coal from Harrison County, Ohio), PSOC 282 (Illinois #6 coal from Jefferson County, Illinois), and PSOC 230 (Rosebud coal from Rosebud County, Montana) were chosen for the combustion tests. The combustion tests included three samples of the raw coals ground to -200 mesh, three samples of coal subjected to chlorinolysis treatment and three samples subjected to chlorinolysis and hydrodesulfurization. The Penn State Fuels and Combustion Laboratory conducted the combustion tests in their plane flame furnace combustion unit using eleven to fifteen pounds of coal for each test. The final report includes a descriptions of the laboratory screening tests for coal processing, the batch reactor production of test coals, and the combustion of test evaluation of the raw and processed coals.

II. Summary

This is the final report for the "Coal Desulfurization by Chlorinolysis-Production and Combustion Test Evaluation of Product Coals," conducted under DoE Interagency Agreement DE-AI01-77ET12547, Mod. A007 for the period September 1, 1981 through April 30, 1982. The work was conducted by the Jet Propulsion Laboratory of the California Institute of Technology at Pasadena, California and the Fuels and Combustion Laboratory of the Pennsylvania State University at University Park, Pennsylvania.

The scope of work consisted of: (1) Equipment modification and preparation for lab-scale and bench-scale testing and production of desulfurized coals, (2) Laboratory-scale screening tests to determine chlorination and hydrodesulfurization conditions for production of desulfurized coals, (3) Bench-scale batch reactor production of chlorinolysis and hydrodesulfurized coals for combustion testing, (4) Combustion testing of two bituminous (PSOC 276, 282) and one sub-bituminous (PSOC 230) coals as: unprocessed coal ground to -200 mesh; chlorinolysis processed coals; and chlorinolysis-hydrodesulfurized coals.

The principal equipment modifications consisted of: (1) Increasing the operating capacity of the bench-scale batch reactor system from two to three kilo grams of coal and installing a Tylan mass flowmeter for more accurate monitoring and control of chlorine flowrates, (2) Modification of the bench-scale dechlorinator from an atmospheric pressure dechlorinator with nitrogen to hydrodesulfurization operation with up to three kilograms of coal at hydrogen pressures up to 100 psig and temperatures up to 700°C.

Laboratory-scale screening tests with PSOC 276 coal were used to investigate: (1) The effect of partially chlorinated coals (Cl_2/S at 2, 4, 8) on coal hydrodesulfurization; (2) The effect of increased hydrogen pressure on assisting hydrodesulfurization; (3) The effects of temperature on hydrodesulfurization and attendant loss of coal volatiles and hydrogen. Test results indicated: (1) Partially chlorinated coals (Cl_2/S of 2, 4) were less hydrodesulfurized than more fully chlorinated coals (Cl_2/S of 8); (2) increased hydrogen pressure from 0 to 100 p.s.i.g. had no apparent impact on chlorinated coal hydrodesulfurization conducted at 700°C and 60 minutes; (3) temperatures of 600-700°C were required to achieve substantial (75-90%) hydrodesulfurization but with attendant high reductions of volatiles (80%) and hydrogen (60%).

Production of chlorinolysis and chlorinolysis-hydrodesulfurized processed coals for combustion tests was carried out in the bench-scale batch reactor equipment. Eleven to fifteen pounds each of PSOC 276, 282 and 230 coals were produced using 3-4 batches per coal at three kilograms of coal feed per batch. Chlorination conditions were: Cl_2/S -6.56, 20-50°C, 0-10 p.s.i.g., 60 minutes, water/coal-1.5, -200 mesh coal. Dechlorination conditions were: 2-3 kilograms of coal per batch, 400°C, 10 SCFH nitrogen, 10-20 p.s.i.g., 60 minutes. Hydrodesulfurization conditions were: 2-3 kilograms of coal per batch, 625-650°C, 10 SCFH hydrogen, 5-50 p.s.i.g., 60-120 minutes.

Coal shipped to the Penn State Fuels and Combustion Laboratory for combustion test evaluation consisted of PSOC 276, 282 and 230 coals as: 30 pounds each of unprocessed coal ground to -200 mesh; 15-16 pounds each of chlorinolysis processed coals; and 11.5-14 pounds each of chlorinolysis-hydrodesulfurized coals.

The Penn State Combustion tests were carried out in a plane flame furnace with coal feed rates of 8-10 pounds per hour. The combustion test results indicated that: (1) The raw coals burned as premium grade coals; (2) Chlorinolysis processed coals had a slight delay in ignition, and slightly lower burning rates than the raw coals but otherwise burned very well to complete burnout; (3) The chlorinolysis-hydrodesulfurized coals had a more difficult ignition than chlorinolysis processed coals and burned more slowly but burned to completion without difficulty. All of the coals burned much better than would be expected from the reduced volatiles content. A possible explanation is that the increased open pore volume of devolatilized coals compensates in part for the loss of volatiles in coal combustion.

III. Conclusions and Recommendations

1. The coal combustion tests conducted by the Penn State Fuels and Combustion Laboratory in their "plane flame furnace" demonstrated that coals desulfurized by the JPL "Chlorinolysis" and "Chlorinolysis-hydrodesulfurization" processes burned satisfactorily to complete burn-out. Some ignition difficulties and reduced burning rates were experienced for the more highly devolatilized coals obtained from the hydrodesulfurization process. However, all of the processed coals burned much better than expected based on the reduced volatiles content. This may be explained in part by the greater open pore volume exhibited by devolatilized coals, which compensates in part for the reduction in coal volatiles.

2. The chlorinolysis process provides a 60-70% desulfurization for high sulfur (>2 wt.%) bituminous coals and a more limited desulfurization of 30-50% for low sulfur (<1%) subbituminous coals. The dechlorination of the chlorinolysis-processed coals at 400°C results in a reduction in coal volatiles (26-37%) and hydrogen (19-31%). Heating values of the chlorinolysis processed coals increase slightly.

3. Chlorinolysis-hydrodesulfurized coals provide an 80-90% desulfurization with hydrodesulfurization at 600-700°C with a reduction in volatiles of 70-80% and hydrogen of 50-60%. Coal heating values increase for all coals with a substantial reduction in oxygen content.

4. Coal chlorination appears to be a necessary pretreatment to achieve maximum desulfurization with hydrodesulfurization. Partial chlorination at 25-50% of stoichiometric Cl_2/S for high sulfur bituminous coals (PSOC 276, 282) does not achieve good hydrodesulfurization results. Approximately stoichiometric Cl_2/S values are required for high sulfur coals. Low-sulfur bituminous coals (PSOC 230) may require greater than stoichiometric Cl_2/S values to achieve maximum desulfurization with chlorinolysis and hydrodesulfurization.

5. Provisions must be made for recovery of coal volatiles in both the dechlorination and hydrodesulfurization coal processing steps. Coal volatiles may represent up to 20-30% of the coal lost in the chlorinolysis process and 30-40% of the coal lost in the hydrodesulfurization process.

6. An experimental study is required of the coal volatiles lost in the dechlorination/hydrodesulfurization steps as a means of identifying the amounts and composition of coal volatiles with the processing conditions of time, temperature, pressure and purge gases. Experimental data on coal volatile losses is necessary to design the necessary process recovery and treatment equipment. The recovered coal volatiles may be used independently of the processed coal as a medium to high B.t.u. gas and/or in conjunction with the processed coal for industrial and utility boilers.

7. The JPL Coal Desulfurization Process can be operated either as a chlorinolysis process or a chlorinolysis-hydrodesulfurization process by appropriate design of the dechlorination stage to accommodate hydrodesulfurization. The major differences between dechlorination and hydrodesulfurization operations is in the operating temperatures (400°C vs 600-700°C) and the amount and composition of volatiles recovery. Hydrogen could be used in the low temperature dechlorination stage in lieu of the nitrogen purge.

8. Physical beneficiation as a pretreatment of coals for reduction of sulfur and ash should be undertaken prior to chlorinolysis treatment as a means of reducing overall process costs and improving the quality of the processed coals.

9. The choice of coal desulfurization processes for given coals, whether "Chlorinolysis" or "Chlorinolysis-hydrodesulfurized," should be based on the requirements for desulfurization indicated by the choice of coals and attendant Federal and State air pollution regulations. The "Chlorinolysis" process provides for a minimum treatment of the coal and should therefore be used unless greater coal desulfurization is required. The hydrodesulfurization stage can also be tailored to provide a gradient of increased coal desulfurization with increasing losses of volatiles as the hydrodesulfurization temperature is increased.

10. Processing conditions for the chlorination process are well established. Hydrodesulfurization processing of the chlorinated coals is a much more recent development and requires extensive process development.

11. Thermal dechlorination of chlorinated coals has been successfully demonstrated on a laboratory-scale but requires further development on a bench-scale level to achieve acceptable levels of residual chlorides, comparable to that present in unchlorinated coal.

12. Further chlorinolysis process development is required to incorporate waste stream processing and HCl recovery from the waste stream for sale and/or reconversion by the Kel-chlor process to chlorine for reuse. A major change will be the incorporation of a waste stream recycle to increase both HCl and H_2SO_4 concentration in the chlorination and waste stream treatment. A beneficial effect will be the increased solubilization and removal of ash from the processed coal.

IV. Experimental Equipment and Operating Procedure

A. Laboratory-Scale Equipment

The laboratory-scale equipment for conducting preliminary screening tests of the coal chlorination and subsequent dechlorination and/or hydrodesulfurization are shown in Figures 1 and 2.

The laboratory-scale tests were carried out with 100-200 grams of -200 mesh coal and 200-400 grams of water in a 500 ml round bottom flask equipped with a glass stirrer and glass fritted disc injector for gaseous chlorine into the coal slurry. Chlorination conditions were for 30-60 minutes at chlorine/sulfur weight ratios of 2, 4 and 8, and a temperature of 50°C. A chlorine/sulfur weight ratio of 8 is approximately stoichiometric for the conversion of sulfur from a -1 valence state to a +6 valence state.

Coal slurries from the chlorination were filtered in a Buchner funnel using Whatman No. 1 filter paper. The filtration wash was carried out with water at 20°C with 2 spray washes using 2 parts of water to 1 part of coal.

Laboratory-scale dechlorinations and hydrodesulfurizations were carried out in a one-inch diameter quartz tube using three to five gram samples, at times of 60 to 120 minutes and temperatures of 400 to 700°C using flow rates of nitrogen or hydrogen of 90 Scm³/min., and a tube rotation of 2 RPM. The normal procedure was to bring the muffle furnace up to the designated operating temperature and then to insert the quartz tube containing the coal into the furnace. The air contained in the quartz tube is rapidly purged with nitrogen. After the designated dechlorination time, the quartz tube is removed from the furnace, cooled with the continuing nitrogen purge and then removed to a closed glass container for subsequent analysis.

The procedure for hydrodesulfurization is approximately the same except that the temperature level is in the range of 500 to 700°C and hydrogen replaces nitrogen. Nitrogen is used to first purge the quartz tube before the hydrodesulfurization and also to purge the hydrogen from the quartz tube at completion of the test. All laboratory-scale tests of dechlorination and hydrodesulfurization were carried out at atmospheric pressure. The bench-scale dechlorinator/hydrodesulfurizer was used frequently in place of the quartz tube even in conjunction with laboratory-scale chlorinations. The bench-scale unit was capable of handling larger coal samples (greater than the 5-gram sample capacity of the quartz tube) up to 3 kilograms of coal and was also equipped to operate at up to 100 p.s.i.g. hydrogen or nitrogen pressure.

B. Bench-Scale Batch Reactor System

1. Chlorinator

The bench-scale batch reactor for chlorination of the coal is shown in the equipment schematic, Figure 3. Nominally the reactor was designed for operation at 2 kilograms of coal and 4 kilograms of water. However, to increase the amount of coal processed per run, the water to coal ratio was reduced from 2/1 to 1.5/1.0 and the amount of coal increased to 3 kilograms.

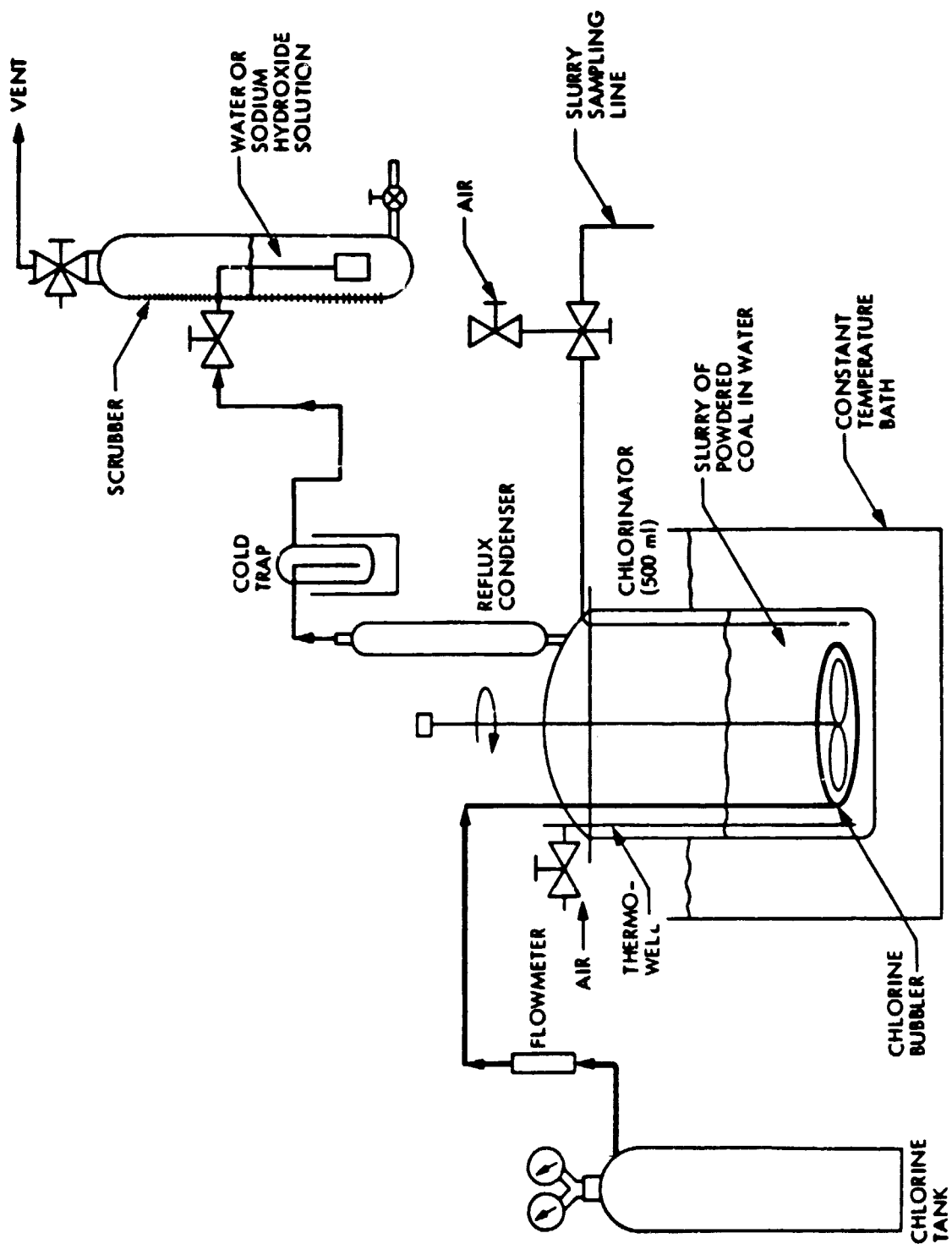


Figure 1. Laboratory Glassware Apparatus for Chlorination of Coal

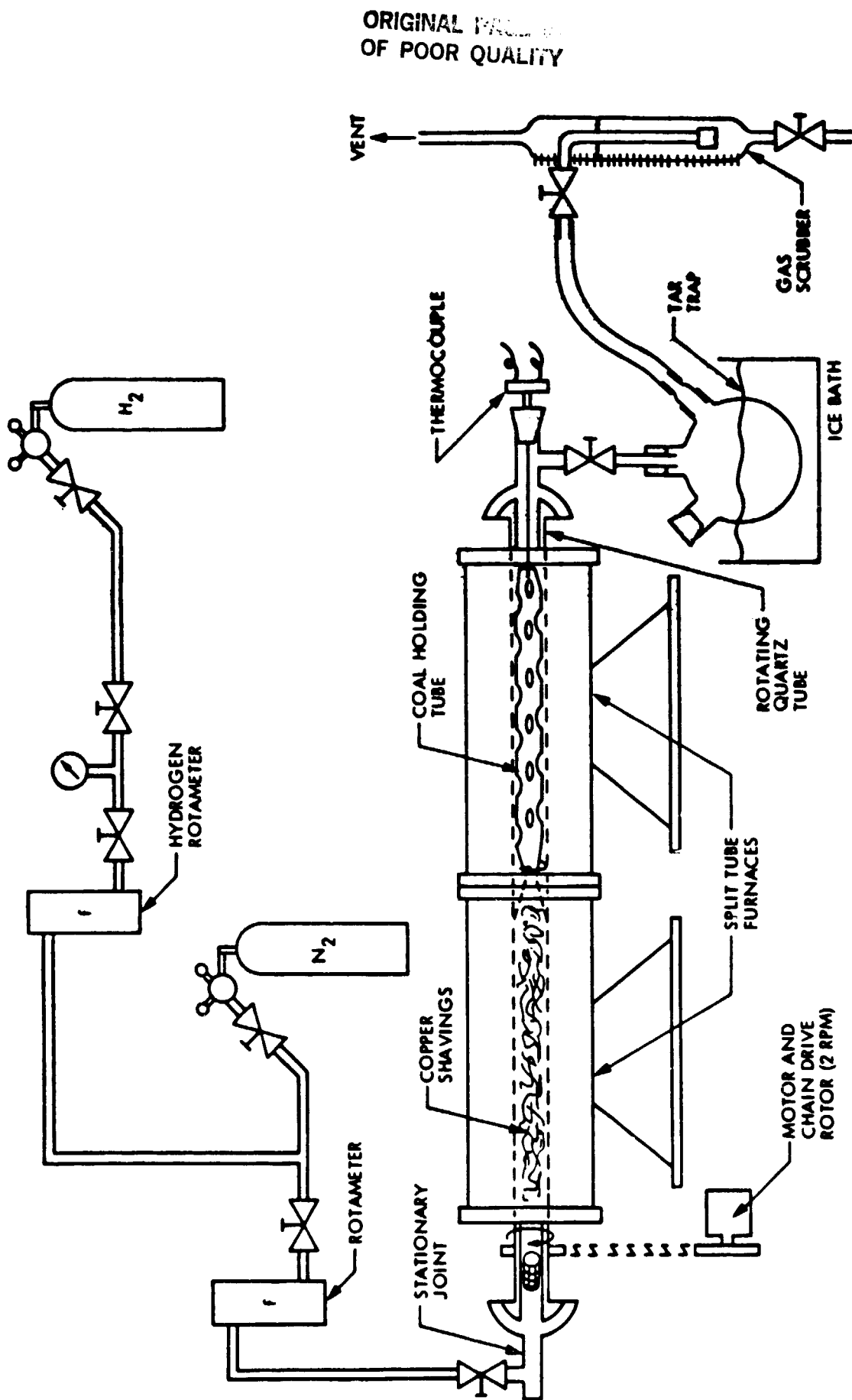


Figure 2. Laboratory Scale Apparatus for Coal Dechlorination and Hydrodesulfurization

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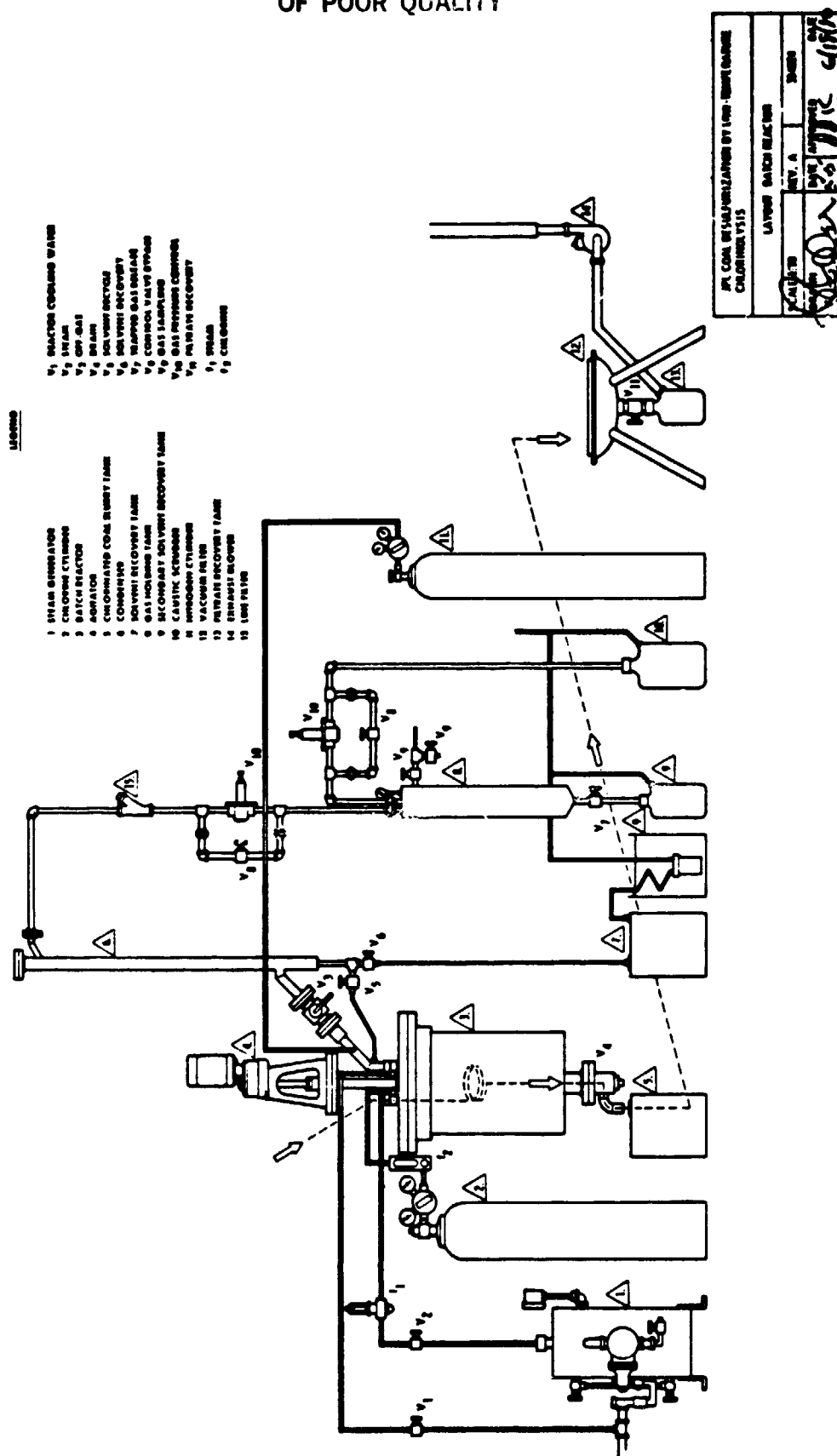


Figure 3. Batch Reactor Equipment System

Thus the overall charge of coal-water slurry was increased from 6 kilograms to 7.5 kilograms but with a 50% increase in coal capacity. Laboratory tests of the increased coal concentration prior to use in the reactor indicated no problems in handling or mixing.

Normal operation of the chlorinator involved charging of the reactor with the coal slurry followed by gaseous chlorine feed to the reactor to provide a stoichiometric amount of chlorine to sulfur in order to convert the pyritic and organic sulfur to sulfuric acid. The stoichiometric amount of chlorine to sulfur is approximately 8 to one by weight. With the increase of coal charged to the reactor, a proportional increase of chlorine flow was required to maintain a stoichiometric ratio for a given reaction time. An initial test with PSOC 276 coal indicated that for a reaction time of 60 minutes, the stoichiometric flow of chlorine to the reactor was slightly in excess of the capacity of the coal slurry to absorb all of the chlorine without chlorine being vented to the ullage space with pressurization of the reactor. Since the chlorine passing through the coal slurry served no purpose, the chlorine flow was reduced to 82% of stoichiometric flow, 4.0 liters per minute. Under these chlorine injection conditions there was no significant reactor pressurization during the 60-minute reaction period with the reactor operated as a closed system. This standard of 82% of stoichiometric flow was used for all of the coals. Chlorine flow was monitored and controlled by a Tylan Mass Flow Controller.

Reactor temperature was kept at ambient temperature (20°C) to start. The reactor was allowed to heat up to 50°C from the exothermic heat of the chlorination reaction. At 50°C, cooling water was introduced into the reactor cooling coils in order to limit the temperature to 50°C. Pressure was generally at atmospheric pressure or slightly above, at 5 to 10 p.s.i.g..

Minor problems of chlorine line filters getting plugged and coal slurry plugging the chlorine injection line aborted two of the runs. However, the majority of runs went without incident.

2. Filtration-wash

The batch vacuum filtration unit constructed from an 18-inch diameter, 2:1 elliptical tank head equipped with a 325 mesh polypropylene filtration cloth and an exhaust blower to provide 20-30 inches of water column vacuum served for filtering and washing the coal slurry after it was drained from the reactor. Since the amount of coal was increased from 2 to 3 kilograms per batch, filtration and wash occurred in two stages since the filtration unit was limited to 2 kilograms of coal capacity. The coal was spray washed manually with two spray washes of water at 20°C using 2 parts of water per one part of coal for each wash. Although a single spray wash was considered to be adequate, a second spray wash was used to insure that no sulfates remained in the coal.

3. Dechlorinator-Hydrodesulfurizer

An equipment schematic of the dechlorinator-hydrodesulfurizer is shown, Figure 4. The bench-scale dechlorinator from the phase 3 work was modified to allow pressure operation up to 100 p.s.i.g. using either hydrogen or nitrogen. The major equipment modification was to provide mechanical seals that could

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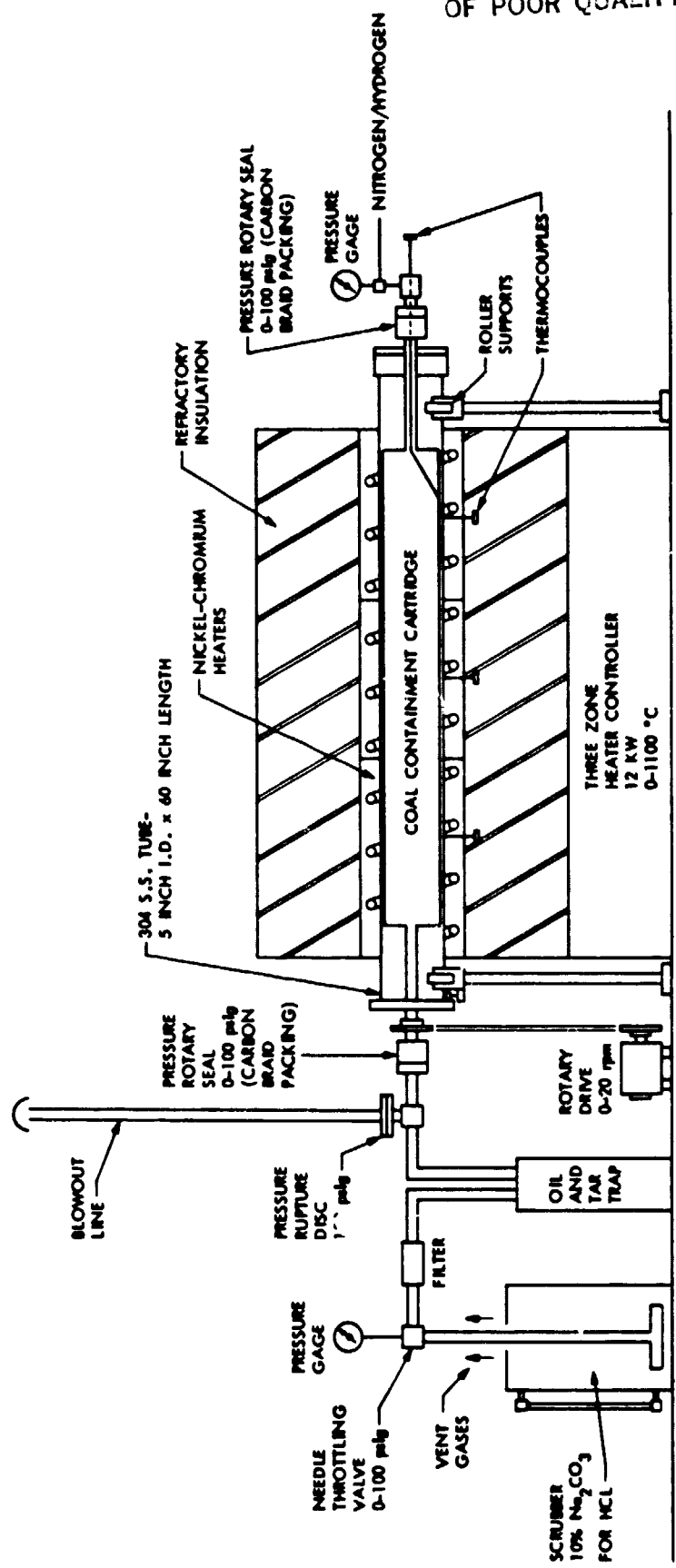


Figure 4. Dechlorinator/Hydrodesulfurizer

contain the hydrogen under pressure while the coal containment cartridge rotated at 3-4 RPM in the furnace at temperatures up to 700°C. A number of mechanical seals were investigated and rejected as inadequate for containing hydrogen gas under rotary seal conditions.

The seals that were finally installed and successfully used consisted of "stuffing boxes" equipped with braided carbon packing that provided a gas-tight seal around the rotating inlet and outlet tubes fixed at each end of the coal canister. The coal canister is 5-inch diameter by 5-1/2 feet long with 2-inch diameter tubes at each end for inlet and outlet gases. The stuffing boxes are recessed away from the furnace to avoid high temperatures on the packing. The rotating tube is enclosed in a Lindberg furnace divided into three longitudinal segments operated by separate heater controls. The furnace is equipped for operation up to 1100°C. A thermocouple installed inside the rotating tube and in contact with the coal provides a direct measurement of coal temperature within the unit. The furnace control thermocouples are on the outside wall of the rotating tube.

The unit is equipped with a carbon rupture disc, rated at 150 p.s.i.g. A trap is included downstream of the coal tube for trapping tars and oils. The trap is under the operating pressure. A needle valve downstream of the trap provides for throttling of the purge gases through a 10% sodium carbonate solution to the atmosphere. The sodium carbonate scrubs the HCl coming from the chlorinated coal.

Dechlorinations were carried out generally at 400°C, atmospheric pressure and rotation of the coal container at 3 to 4 R.P.M. with 10 SCFH of nitrogen purge for 60 minutes. The coal container can accommodate up to 3 kilograms of coal when 50% full. Laboratory-scale quantities of 100 to 200 grams of chlorinated coal were placed in stainless steel tubes measuring 1-3/8-inch diameter by 2-feet and equipped with end closures of 325-mesh stainless steel screen. Up to three tubes could be placed in the coal containment cartridge at one time which allowed multiple coal samples to be dechlorinated or hydrodesulfurized simultaneously. The advantage of this approach for laboratory-scale samples was that a much larger sample could be accommodated for treatment, whereas the quartz tube was limited to less than 10 grams.

Hydrodesulfurization of the coals was generally conducted at 500 to 700°C, 0 to 100 p.s.i.g., with hydrogen flow at 10-25 SCFH for 60 to 120 minutes. Tube rotation was generally at 3-4 RPM. Laboratory-scale tests were with approximately 100 gram quantities of coal. Tests with batch reactor quantities of coal were with 2 to 3 kilograms of coal per batch.

In order to improve the contact of hydrogen and coal, flights were installed in the coal container for hydrodesulfurization with coals PSOC 282 and PSOC 230 for runs 26-2/3/82 through runs 33-2/19/82. The flights consisted of four, three-foot long by 1-1/4-inch wide, 1/8-inch thick mild steel strips anchored to two diagonal steel cross pieces at each end to position the flights 90° apart. The flights were anchored within the coal container with a set screw that could be loosened to remove the flights. The use of the flights provided large losses of coal fines into the downstream trap, especially with PSOC 230 coal.

V. Laboratory-Scale Screening Tests

A. Chlorination

Laboratory-scale test runs were carried out with PSOC 276 coal using 100-200 grams of -200 mesh coal and 200-400 grams of water. Chlorination conditions were for 30-60 minutes at chlorine/sulfur flow rates of 2/1, 1/1, and 8/1 at a temperature of 50°C. The chlorination was followed by a coal slurry filtration and spray wash with water at 20°C using 2 washes at a water to coal ratio of 2. The experimental operating data is included as runs 1-6, Table 1.

B. Dechlorination/Hydrodesulfurization

The combined dechlorination and hydrodesulfurization of the chlorinated coal samples was carried out for run 1 in the lab scale, one-inch diameter quartz tube. The remaining runs, 2-6 were treated in the bench-scale unit using the 1-3/8 inch diameter by 2-foot long tubes for containing the chlorinated coal samples, up to 100 grams per tube.

C. Desulfurization

Run 1

The PSOC 276 chlorinated coal from run 1 was treated with hydrogen at 90 $\text{Scm}^3/\text{minute}$ for 120 minutes at 600°C. Leco analysis indicated a total sulfur removal of 75% (average of 2 analyses) with a residual chlorine level of 0.2 wt.%.

Runs 2-6

Runs 3-5 were hydrodesulfurized at 700°C and 100 p.s.i.g. with 25 SCFH hydrogen flow for 60 minutes. (Run 2 was abandoned because of incorrect chlorine flows). Hydrogen was used at 100 p.s.i.g. in order to find whether increased hydrogen pressure would provide increased and/or more rapid hydrodesulfurization. Runs 3 and 4 which were chlorinated at Cl_2/S values of 2 and 4 respectively showed 62 and 64% total sulfur removal. Run 5 at a Cl_2/S value of 8 showed 83% total sulfur removal (Table 1). A tentative conclusion from these 3 runs is that partial chlorination (25 and 50% of stoichiometric Cl_2 to sulfur values) does not show high sulfur removal in conjunction with hydrodesulfurization. Also, the use of hydrogen at 100 p.s.i.g. does not appear to improve hydrodesulfurization over that obtained under atmospheric pressure in phase III (ref. 2).

Run 6 coal was chlorinated at a Cl_2/S value of 2. The chlorinated coal sample was divided into three parts and then hydrodesulfurized at 500, 550 (aborted at 10 minutes) and 600°C, and 100 p.s.i.g. for 60 minutes. Originally, the anticipation was that partial chlorination, as low as 25% of the stoichiometric Cl_2/S value, would be adequate in assisting hydrodesulfurization to achieve high sulfur removal. Run 6 hydrodesulfurization data shows relatively low sulfur removals of 49-62%. The probable explanation is that the limited chlorination (25% of stoichiometric Cl_2/S) and low hydrodesulfurization temperatures of 500-600°C are responsible for the low desulfurization.

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| RUN-DATE ^e | FEED COAL | | | | | | CHLORINATION | | | | | FILTRATION/WASH | | | | DECHLORINATION/HYDRO | | | | | |
|-----------------------|---|------|--------------------------|---------------|------|-------|------------------|----------------------------|---------------|--------------|--------------------|-----------------|-----------------|------------------------|--------------------------------------|----------------------|-------------------------|--------------|----------------|-------------------|--------------|
| | COAL | | | SULFUR (WT.%) | | | WATER (GRAMS) | Cl ₂ (g/MTN) | TIME (MIN) | TEMP (°C) | Cl ₂ /S | FILTER CAKE | | | COAL ^f RECOVERY (%) | RUN | COAL FEED (GRAMS) | TEMP (°C) | GAS | | |
| | TYPE* (PSOC) | MESH | AMOUNT DRY (GRAMS) | PYR | ORG | TOTAL | | | | | | WATER/ COAL | WATER (WT.%) | COAL DRY (GRAMS) | | | | | TYPE | FLOW (SCFH) | PRE (PSI) |
| 1-8/23/81 | 276 | -200 | 100 | 2.63 | 1.17 | 3.95 | 200 | 0.30 | 30 | 50 | 4 | 4 | - | - | - | - | 3.70 ^a | 600 | H ₂ | 0.09 ^a | 0 |
| 3-11/11/81 | 276 | -200 | 100 | 2.63 | 1.17 | 3.37 | 200 | 0.09 | 30 | 50 | 2 | 2@2/1 | 23.3 | 93 | 93 | - | 93 | 700 | H ₂ | 25 | 100 |
| 4-11/12/81 | 276 | -200 | 100 | 2.63 | 1.17 | 3.87 | 200 | 0.18 | 30 | 50 | 4 | 2@2/1 | 27.9 | 101 | 101 | - | 101 | 700 | H ₂ | 25 | 100 |
| 5-11/12/81 | 276 | -200 | 100 | 2.63 | 1.17 | 3.87 | 200 | 0.18 | 60 | 50 | 8 | 2@2/1 | 28.5 | 103 | 103 | - | 103 | 700 | H ₂ | 25 | 100 |
| 3A-11/17/81 | ACID WASH 30 GRAMS COAL FROM RUN 3-11/11/81 WITH 500 ML OF 10% HCl, STIRRED FOR 60 MINUTES AT 90°C, FILTRATION AND WASH TWICE WITH 20 | | | | | | | | | | | | | | | | | | | | |
| 4A-11/17/81 | ACID WASH 30 GRAMS COAL FROM RUN 4-11/12/81 WITH 500 ML OF 10% HCl, STIRRED FOR 60 MINUTES AT 90°C, FILTRATION AND WASH TWICE WITH 20 | | | | | | | | | | | | | | | | | | | | |
| 5A-11/17/81 | ACID WASH 30 GRAMS COAL FROM RUN 5-11/12/81 WITH 500 ML OF 10% HCl, STIRRED FOR 60 MINUTES AT 90°C, FILTRATION AND WASH TWICE WITH 20 | | | | | | | | | | | | | | | | | | | | |
| 6-11/19/81 | 276 | -200 | 200 | 2.63 | 1.17 | 3.37 | 400 | 0.18 | 30 | 50 | 2 | 2@2/1 | 21.9 | 197 | 98 | 6A | 66 | 500 | H ₂ | 25 | 100 |
| | | | | | | | | | | | | | | | | 6B | 66 | 550 | H ₂ | 25 | 100 |
| | | | | | | | | | | | | | | | | 6C | 66 | 600 | H ₂ | 25 | 100 |
| 9-12/3/81 | PGH.#8 | -200 | 200 | 0.35 | 0.77 | 1.12 | 400 | 0.28 | 60 | 50 | 8 | 2@2/1 | 1.2 | 225 | 112 | - | 223 | 500 | H ₂ | 25 | 100 |
| 10-12/9/81 | ILL.#6 | -200 | 200 | 0.76 | 1.71 | 2.76 | 400 | 0.30 | 60 | 50 | 8 | 2@2/1 | 2.9 | 231 | 115 | - | 229 | 500 | H ₂ | 25 | 100 |
| 11-12/9/81 | EAGLE#5 | -200 | 200 | 0.00 | 0.49 | 0.49 | 400 | 0.046 | 60 | 50 | 8 | 2@2/1 | 2.1 | 202 | 101 | - | 201 | 500 | H ₂ | 25 | 100 |
| 14-12/17/81 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.87 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | | | | 9 | 1865 | 400 | N ₂ | 10 | 10- |
| 15-12/18/81 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.87 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | 9.2 | 9036 | 100 | 10 | 1965 | 400 | N ₂ | 10 | 10- |
| 16-12/21/81 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.37 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | | | | 11 | 2651 | 400 | N ₂ | 10 | 10- |
| | | | | | | | | | | | | | | | | 12 | 2555 | 400 | N ₂ | 10 | 10- |
| | | | | | | | | | | | | | | | | TOTAL 9036 | | | | | |
| 17-1/7/82 | 282 | -200 | 3000 | 0.43 | 0.75 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | | | | 13 | 3237 | 400 | N ₂ | 10 | 10- |
| 18-1/7/82 | 282 | -200 | 3000 | 0.43 | 0.75 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | 31.5 | 8730 | 93 | 14 | 2670 | 400 | N ₂ | 10 | 10- |
| 19-1/8/82 | 282 | -200 | 3000 | 0.43 | 0.75 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | | | | 15 | 2374 | 400 | N ₂ | 10 | 10- |
| | | | | | | | | | | | | | | | | TOTAL 8780 | | | | | |
| 20-1/14/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 25.9 | 2701 | 90 | 16 | 2701 | 400 | N ₂ | 10 | 10- |
| 21-1/14/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 38.9 | 2801 | 93 | 17 | 2801 | 400 | N ₂ | 10 | 10- |
| 22-1/18/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 14.4 | 2938 | 98 | 18 | 2938 | 400 | N ₂ | 10 | 10- |
| | | | | | | | | | | | | | | | | TOTAL 8440 | | | | | |
| 23-1/22/82 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.87 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | 28.5 | 3201 | 107 | 19 | 3201 | 650 | H ₂ | 10 | 5-10 |
| 24-1/26/82 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.87 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | 15.9 | 3310 | 110 | 20 | 3310 | 650 | H ₂ | 10 | 5-10 |
| 25-1/26/82 | 276 | -200 | 3000 | 2.63 | 1.17 | 3.87 | 4500 | 4.00 | 60 | 20-50 | 6.56 | 2@2/1 | 32.0 | 3201 | 107 | 21 | 3201 | 650 | H ₂ | 10 | 5-10 |
| | | | | | | | | | | | | | | | | TOTAL 9712 | | | | | |
| 26-2/3/82 | 282 | -200 | 3000 | 0.43 | 0.73 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | 15.9 | 2933 | 98 | 24 | 2933 | 632 | H ₂ | 10 | 50 |
| 27-2/4/82 | 282 | -200 | 3000 | 0.43 | 0.73 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | 12.4 | 2978 | 99 | 23 | 2978 | 632 | H ₂ | 10 | 50 |
| 32-2/17/82 | 282 | -200 | 3000 | 0.43 | 0.73 | 1.54 | 4500 | 1.59 | 60 | 20-50 | 6.56 | 2@2/1 | 10.2 | 3005 | 100 | 28 | 3005 | 635 | H ₂ | 10 | 50 |
| | | | | | | | | | | | | | | | | TOTAL 8916 | | | | | |
| 29-2/15/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 22.6 | 2756 | 92 | 25 | 2756 | 645 | H ₂ | 10 | 50 |
| 30-2/15/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 40.2 | 2720 | 91 | 26 | 2720 | 640 | H ₂ | 10 | 50 |
| 31-2/16/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 23.7 | 2751 | 92 | 27 | 2751 | 640 | H ₂ | 10 | 50 |
| 33-2/19/82 | 230 | -200 | 3000 | 0.35 | 0.52 | 0.87 | 4500 | 0.90 | 60 | 20-50 | 6.56 | 2@2/1 | 0.3 | 2683 | 90 | 29 | 2683 | 625 | H ₂ | 10 | 50 |
| | | | | | | | | | | | | | | | | TOTAL 10910 | | | | | |

- NOTES: a - LABORATORY SCALE - DECHLORINATION IN 1-INCH DIAM. QUARTZ TUBE. FLOW IN LITERS/MINUTE.
b - ANALYSIS: S-SULFUR FORMS, P-PROXIMATE, U-ULTIMATE
c - FLANGE GASKET ON HYDRODESULFURIZER BLEW AND RUN STOPPED AT 10 MINUTES
d - COAL PLACED IN 1-1/4-INCH DIAMETER x 2-FOOT LONG S.S. TUBES FOR HYDRODESULFURIZATION IN BENCH-SCALE UNIT.
e - RUNS 7, 8 RERUN AS RUNS 10, 11 BECAUSE OF HYDRO DESULFURIZING PROBLEMS; RUNS 12 AND 13 ABORTED DUE TO CHLORINATOR PROBLEMS OF Cl₂ FLOW; RUN 23 ABORTED IN HYDRODESULFURIZATION AND RERUN 2 DAYS LATER. RUN 27 ABORTED IN HYDRODESULFURIZER AND RESTARTED SAME DAY; RUN 28 HAD COAL CANISTER SPILL COAL DURING HYDRODESULFURIZATION, RERUN AS RUN 32; RUNS 30 AND 31 HAD LARGE AMOUNTS OF DRY COAL IN TRAP EXPLAINING LARGE LOSSES OF COAL.
f - Cl₂ ADDITION TO COAL INCREASES RECOVERY TO OVER 100% SINCE Cl₂ WEIGHT CORRECTION WAS UNAVAILABLE. SIGNIFICANT LOSSES OF 230 COAL NOTED IN FILTRATION PROBABLY DUE TO SMALL MESH SIZE.
g - SULFUR ON A DRY BASIS.
h - FLIGHTS INSTALLED FOR HYDRODESULFURIZATION OF PSOC 282 AND 230 COALS.

*PSOC276 - PITTSBURGH COAL FROM HARRISON COUNTY, OHIO; GEORGETOWN NO. 24 MINE
PSOC282 - ILLINOIS #6 COAL FROM JEFFERSON COUNTY, ILLINOIS; ORIENT NO. 6 MINE WASHED
PSOC230 - ROSEBUD COAL FROM ROSEBUD COUNTY, MONTANA; ROSEBUD COLSTRIP FIELD
PGH #8 COAL FROM GREENE COUNTY, PA.; AMWAY RESOURCES EMERALD MINE, WAYNESBURG, PA.
ILL. #6 COAL FROM JACKSON COUNTY, ILL.; CONSOLIDATION COAL CO, BURNING STAR MINE #2, CARBONDALE, ILL.
EAGLE #5 COAL FROM MOFFAT COUNTY, COLO.; EMPIRE ENERGY CO. MINE, CRAIG, COLO.

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Table 1. Coal Desulfurization by Chlorinolysis Experimental Data

| DECHLORINATION/HYDRODESULFURIZATION | | | | | | | | PRODUCT COAL | | | | | | | | REMARKS |
|--|-------------------------|--------------|----------------|-------------------|------------------|-----------------|---------------------------|--------------------------------------|---------------------|------------|--------|------------|--------|------------|--------------------|--|
| NO. | COAL FEED (GRAMS) | TEMP (°C) | GAS | | | TIME (MIN) | COAL OUTPUT (GRAMS) | COAL ^u RECOVERY (%) | SULFUR ^g | | | | | | CHLORINE (WT.%) | |
| | | | TYPE | FLOW (SCFH) | PRESS. (PSIG) | | | | PYR. | | ORG | | TOTAL | | | |
| | | | | | | | | | (WT.%) | REM (%) | (WT.%) | REM (%) | (WT.%) | REM (%) | | |
| | 3.70 ^a | 600 | H ₂ | 0.09 ^a | 0 | 120 | 2.36 | 64 | - | - | - | - | 0.98 | 75 | 0.24 | LAB. RUN, LECO ANAL. |
| | 93 | 700 | H ₂ | 25 | 100 | 60 | 60 | | 0.06 | 98 | 1.42 | -26 | 1.48 | 62 | <0.05 | LAB SCALE CHLORINATION, HYDRODESULFURIZATION IN BENCH-SCALE UNIT. ^d |
| | 101 | 700 | H ₂ | 25 | 100 | 60 | 60 | | 0.05 | 98 | 1.36 | -16 | 1.41 | 64 | 0.07 | |
| | 103 | 700 | H ₂ | 25 | 100 | 50 | 61 | | 0.05 | 98 | 0.61 | 48 | 0.66 | 83 | <0.05 | |
| STRATION AND WASH TWICE WITH 200 ML WATER. | | | | | | | | | | | | | | | | |
| STRATION AND WASH TWICE WITH 200 ML WATER. | | | | | | | | | | | | | | | | |
| STRATION AND WASH TWICE WITH 200 ML WATER. | | | | | | | | | | | | | | | | |
| A | 66 | 500 | H ₂ | 25 | 100 | 60 | 47.4 | 72 | 0.05 | 98 | 1.72 | -47 | 1.77 | 54 | 0.16 | CL ₂ /S LIMITED TO 2/1 BENCH-SCALE HYDRO- DESULFURIZED ^d LAB SCALE CHLORINATION, BENCH-SCALE HYDRO- DESULFURIZATION |
| E | 66 | 550 | H ₂ | 25 | 100 | 10 ^c | 46.8 | 71 | 0.05 | 98 | 1.94 | -66 | 1.99 | 49 | 0.07 | |
| C | 66 | 600 | H ₂ | 25 | 100 | 60 | 41.4 | 63 | 0.04 | 98 | 1.42 | -21 | 1.46 | 62 | 0.05 | |
| | 223 | 500 | H ₂ | 25 | 100 | 60 | 146 | 65 | 0.02 | 94 | 0.40 | 48 | 0.42 | 62 | 0.35 | |
| | 229 | 500 | H ₂ | 25 | 100 | 60 | 149 | 65 | <0.01 | 99 | 1.10 | 36 | 1.10 | 60 | 0.46 | BENCH-SCALE HYDRO- DESULFURIZATION |
| | 201 | 500 | H ₂ | 25 | 100 | 60 | 140 | 70 | <0.01 | - | 0.30 | 39 | 0.30 | 39 | 0.45 | |
| | 1865 | 400 | N ₂ | 10 | 10-20 | 60 | 1211 | 65 | | | | | | | | BATCH REACTOR PRODUCTION OF CHLORINOLYSIS PROCESSED 276 COAL. |
| 0 | 1965 | 400 | N ₂ | 10 | 10-20 | 60 | 1535 | 78 | | | | | | | | |
| 1 | 2651 | 400 | N ₂ | 10 | 10-20 | 60 | 2049 | 77 | | | | | | | | |
| 2 | 2555 | 400 | N ₂ | 10 | 10-20 | 60 | 1835 | 72 | | | | | | | | |
| TAL9036 | | | | | | | 6629 | 73 | 0.14 | 95 | 1.17 | 0 | 1.31 | 66 | 1.13 | BATCH PRODUCTION OF CHLORINOLYSIS PROCESSED 282 COAL |
| 3 | 3237 | 400 | N ₂ | 10 | 10-20 | 60 | 2184 | 68 | | | | | | | | |
| 4 | 2670 | 400 | N ₂ | 10 | 10-20 | 60 | 2315 | 87 | | | | | | | | |
| 5 | 2874 | 400 | N ₂ | 10 | 10-20 | 60 | 2334 | 81 | | | | | | | | |
| TAL6780 | | | | | | | 6833 | 78 | 0.15 | 65 | 0.53 | 29 | 0.68 | 56(69) | 2.86 | BATCH PRODUCTION OF CHLORINOLYSIS PROCESSED 230 COAL |
| 6 | 2701 | 400 | N ₂ | 10 | 10-20 | 60 | 2179 | 81 | | | | | | | | |
| 7 | 2801 | 400 | N ₂ | 10 | 10-20 | 60 | 2361 | 84 | | | | | | | | |
| 8 | 2938 | 400 | N ₂ | 10 | 10-20 | 60 | 2234 | 81 | | | | | | | | |
| TAL8440 | | | | | | | 6774 | 80 | 0.24 | 31 | 0.38 | 27 | 0.62 | 29 | 0.74 | CHLORINOLYSIS AND HYDRODESULFURIZATION FOR 276 COAL WITHOUT FLIGHTS |
| 9 | 3201 | 650 | H ₂ | 10 | 5-10 | 60 | 1952 | 61 | | | | | | | | |
| 0 | 3310 | 650 | H ₂ | 10 | 5-10 | 120 | 2179 | 66 | | | | | | | | |
| 1 | 3201 | 650 | H ₂ | 10 | 5-10 | 120 | 2238 | 70 | | | | | | | | |
| TAL9712 | | | | | | | 6370 | 66 | 0.04 | 98 | 0.49 | 58 | 0.53 | 86 | 0.50 | CHLORINOLYSIS AND HYDRODESULFURIZATION FOR 282 COAL WITH FLIGHTS |
| 4 | 2933 | 632 | H ₂ | 10 | 50 | 90 | 2107 | 72 | | | | | | | | |
| 3 | 2978 | 632 | H ₂ | 10 | 50 | 90 | 2043 | 69 | | | | | | | | |
| 3 | 3005 | 635 | H ₂ | 10 | 50 | 90 | 1739 | 58 | | | | | | | | |
| TAL8916 | | | | | | | 5888 | 66 | 0.05 | 88 | 0.27 | 64 | 0.32 | 79(85) | 1.59 | CHLORINOLYSIS AND HYDRODESULFURIZATION FOR 230 COAL WITH FLIGHTS |
| 5 | 2756 | 645 | H ₂ | 10 | 50 | 90 | 1703 | 62 | | | | | | | | |
| 5 | 2720 | 640 | H ₂ | 10 | 50 | 90 | 1062 | 39 ^e | | | | | | | | |
| 7 | 2751 | 640 | H ₂ | 10 | 50 | 90 | 1739 | 58 ^e | | | | | | | | |
| 9 | 2683 | 625 | H ₂ | 10 | 50 | 90 | 1457 | 54 | | | | | | | | |
| TAL10910 | | | | | | | 5961 | 55 | 0.01 | 97 | 0.37 | 29 | 0.38 | 56 | 0.49 | |

2. CHLORINATOR PROBLEMS OF CL₂ FLOW;
RESTARTED SAME DAY;
LARGE AMOUNTS OF DRY COAL IN TRAP
SIGNIFICANT LOSSES OF 230 COAL NOTED

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The tentative conclusions reached from runs 1 through 6 with PSOC 276 coal are that chlorine requirements must be near stoichiometric ($\text{Cl}_2/\text{S}=8$) to achieve high coal hydrodesulfurization results. However, Phase III experimental work did show for a few coals, high hydrodesulfurization values at 700°C without any prior coal chlorination (ref. 3).

D. Proximate-Ultimate Analyses

The comparison of Runs 3, 4, and 5 (Table 2) subjected to increasing levels of chlorination, respectively Cl_2/S values of 2, 4 and 8, followed by hydrodesulfurization at 700°C indicated no substantial differences in proximate and ultimate analyses. Volatiles were reduced from 37.2 wt.% in the raw coal to 4-5 wt.% as a result of hydrodesulfurization at 700°C. Heating values for the coal after hydrogen treatment were relatively unchanged. Hydrogen values were reduced from 3.91 wt.% in the raw coal to 0.66-1.48 wt.%. Ash values increased significantly from 11.5 wt.% to 13.2-15.3 wt.% as a result of the loss of volatiles. Oxygen content decreased from 5.87 wt.% to 1.27-1.47 wt.%.

Coal samples 6A, 6B, and 6C obtained from run 6 which was chlorinated at Cl_2/S equal to 2 and then subject to hydrodesulfurization at the respective temperatures of 500, 550 and 600°C showed a strong correlation of coal volatile reduction with increasing temperatures. Coal volatiles were 12.6 wt.% at 500°C, 8.81 wt.% at 550°C and 5.00 wt.% at 600°C. Hydrogen values were 3.22 wt.% at 500°C, 2.54 wt.% at 550°C and 2.06 wt.% at 600°C. Phase III data (ref. 3) indicates that the loss of volatiles and possibly hydrogen in more highly chlorinated coals ($\text{Cl}_2/\text{S} = 8$) may not be as great as in the less chlorinated coals such as that of run 6 at Cl_2/S of 2. This may be attributed in part to the added cross-linking of coal structure obtained from the added chlorination.

E. Acid Wash for Ash Removal

Thirty-gram samples of PSOC 276 coal from runs 3, 4 and 5 were each treated with 500 ml of 10% HCl and stirred in a flask at 90°C for sixty minutes followed by filtration and two washes with 200 ml water, Table 1.

The ash levels were reduced as follows:

| Run | Before Acid Wash | After Acid Wash | Ash Reduction (%) |
|-----|------------------|-----------------|-------------------|
| 3 | 15.3 | 12.1 | 21 |
| 4 | 15.9 | 11.5 | 28 |
| 5 | 13.2 | 11.0 | 17 |

This acid-wash experiment was a preliminary test to determine the extent of additional ash removal that could be obtained by an acid wash of coal that had been subjected to hydrodesulfurization. Normal ash reduction of chlorinolysis processed coal is approximately 25% in the filtrate and wash water after chlorination.

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Table 2. Proximate and Ultimate Analysis of Raw and Processed Coals

| RUN | COAL PSOC** | PROXIMATE ANALYSIS* | | | | | ULTIMATE ANALYSIS* | | | | |
|-----------------|----------------|----------------------|----------------------------|----------------|-----------------|-------------------|---------------------|---------------------|-------------------|---------------------|-------------------|
| | | VOLATILES (WT. %) | FIXED CARBON (WT. %) | ASH (WT. %) | HHV (BTU/LB) | CARBON (WT. %) | HYDROGEN (WT. %) | NITROGEN (WT. %) | SULFUR (WT. %) | CHLORINE (WT. %) | OXYGEN (WT. %) |
| RAW COAL | 276 | 37.2 | 51.3 | 11.5 | 12,755 | 71.6 | 5.67 | 1.28 | 3.91 | 0.16 | 5.87 |
| 3 | 276 | 4.42 | 80.3 | 15.3 | 12,733 | 79.0 | 1.63 | 1.16 | 1.48 | <0.05 | 1.47 |
| 4 | 276 | 4.95 | 79.2 | 15.9 | 12,787 | 78.3 | 1.78 | 1.28 | 1.41 | 0.07 | 1.29 |
| 5 | 276 | 4.21 | 82.0 | 13.2 | 12,964 | 82.0 | 1.63 | 1.71 | 0.66 | <0.05 | 1.27 |
| 6A | 276 | 12.6 | 74.1 | 13.3 | 12,968 | 77.7 | 3.22 | 1.53 | 1.77 | 0.16 | 2.31 |
| 6B | 276 | 8.81 | 75.4 | 15.8 | 12,783 | 76.4 | 2.54 | 1.59 | 1.99 | <0.07 | 1.64 |
| 6C | 276 | 5.00 | 79.8 | 15.2 | 12,925 | 78.3 | 2.06 | 1.29 | 1.46 | <0.05 | 1.76 |
| RAW COAL | PGH#8 | 33.66 | 52.03 | 14.3 | - | 73.4 | 4.88 | 1.42 | 1.12 | - | 4.90 |
| 9 | PGH#8 | 8.79 | 65.20 | 26.0 | 10,931 | 66.0 | 2.49 | 1.22 | 0.42 | 0.35 | 3.48 |
| RAW COAL | ILLINOIS #6 | 37.23 | 51.23 | 11.5 | - | 69.37 | 4.63 | 1.24 | 2.76 | - | 10.46 |
| 10 | ILLINOIS #6 | 9.49 | 80.10 | 10.4 | 13,282 | 82.3 | 2.99 | 1.43 | 1.10 | 0.46 | 1.28 |
| RAW COAL | EAGLE#5 | 39.92 | 52.49 | 7.6 | - | 69.82 | 5.17 | 1.29 | 0.49 | - | 15.71 |
| 11 | EAGLE#5 | 10.80 | 78.90 | 10.8 | 13,233 | 80.5 | 3.02 | 1.61 | 0.30 | 0.45 | 3.28 |
| RAW COAL | 276 | 37.20 | 51.3 | 11.50 | 12,755 | 71.6 | 5.67 | 1.28 | 3.87 | 0.16 | 5.87 |
| 14,15,16 | 276 | 23.50 | 66.6 | 9.88 | 12,792 | 72.7 | 3.93 | 1.46 | 1.31 | 1.13 | 9.62 |
| 23,24,25 | 276 | 6.50 | 84.9 | 8.63 | 13,479 | 84.4 | 2.07 | 1.73 | 0.53 | 0.50 | 2.14 |
| RAW COAL | 282 | 33.80 | 59.50 | 6.70 | 13,092 | 74.8 | 4.82 | 1.69 | 1.54 | 0.47 | 9.92 |
| 17,18,19 | 282 | 25.10 | 67.20 | 7.76 | 13,060 | 77.2 | 3.92 | 1.83 | 0.68 | 2.86 | 5.70 |
| 26,27,32 | 282 | 7.57 | 82.30 | 10.10 | 13,167 | 82.0 | 2.13 | 1.75 | 0.32 | 1.59 | 2.12 |
| RAW COAL | 230 | 38.90 | 52.10 | 9.03 | 11,892 | 69.6 | 4.40 | 1.06 | 0.87 | <0.05 | 14.90 |
| 20,21,22 | 230 | 34.20 | 56.00 | 9.79 | 12,127 | 77.1 | 4.14 | 1.61 | 0.62 | 0.74 | 6.53 |
| 29,30,31, 33 | 230 | 6.25 | 81.80 | 12.00 | 12,524 | 80.9 | 2.14 | 1.20 | 0.38 | 0.49 | 2.82 |

*DRY BASIS

**PSOC276 - PITTSBURGH COAL FROM HARRISON COUNTY, OHIO; GEORGETOWN NO. 24 MINE.

PSOC282 - ILLINOIS #6 COAL FROM JEFFERSON COUNTY, ILLINOIS; ORIENT NO. 6 MINE WASHED.

PSOC230 - ROSEBUD COAL FROM ROSEBUD COUNTY, MONTANA; ROSEBUD COLSTRIP FIELD.

PGH #8 COAL FROM GREENE COUNTY, PA.; ARAWAY RESOURCES EMERALD MINE, WAYNESBURG, PA.

ILL #6 COAL FROM JACKSON COUNTY, ILL.; CONSOLIDATED COAL CO., BURNING STAR MINE #2, CARBONDALE, ILL.

EAGLE #5 COAL FROM MOFFAT COUNTY, COLO.; EMPIRE ENERGY CO. MINE, CRAIG, COLO.

F. Pittsburgh #8 Coal from Greene County, Pa., Ill. #6 Coal from Jackson County, Ill., Eagle #5 Coal from Moffat County, Colo.

1. Coal Desulfurization

The above coals were obtained with an inquiry of how these coals would fare under the coal desulfurization by chlorinolysis process. The coals were included in the laboratory-scale screening tests using stoichiometric flows of chlorine to sulfur ($\text{Cl}_2/\text{S} = 8$) and a dechlorination in the bench-scale reactor at 500°C using 25 SCFH hydrogen (over 200 gram coal samples) at 100 p.s.i.g. for sixty minutes, Table 1. Pittsburgh #8 from Greene County, Pa., showed 62% sulfur reduction from 1.12 wt.% to 0.42 wt.%. Illinois #6 from Jackson County, Ill., showed 60% sulfur reduction from 2.76 wt.% to 1.10 wt.%. Eagle #5 from Greene County, Pa., which had only organic sulfur of 0.49 wt.% showed a 39% sulfur reduction to 0.30 wt.%. The sulfur reduction values were representative of that which would be obtained by the normal chlorinolysis process without benefit of hydrodesulfurization. This was expected in part since the dechlorination temperature was relatively low at 500°C . However, the use of H_2 at 100 p.s.i.g. was originally considered to offer hope for some hydrodesulfurization even at 500°C . The results of desulfurization were reasonably attractive since organic sulfur in all three coals was the predominant species with pyritic sulfur between zero and one-third of the total sulfur.

2. Proximate and Ultimate Analyses

Dechlorination of the Pittsburgh #8 from Greene County, Pa., Illinois #6 from Jackson County, Ill. and Eagle #5 coals from Moffat County, Colo. at 500°C with hydrogen at 100 p.s.i.g. for 60 minutes showed a substantial reduction in volatiles from 33-40 wt.% to 8.8-11.0 wt.%. Hydrogen values were reduced from 4.63-5.00 wt.% to 2.49-2.99 wt.%. Fixed carbon values increased from 51-52 wt.% to 65-80 wt.%. Pittsburgh #8 from Greene County, Pa., showed a high ash to start, 14.33 wt.%, which increased to 26.0 wt.% after dechlorination. The other two coals did not show this high ash increase. In fact, Illinois #6 from Jackson County, Ill., showed an ash decrease from 11.4 wt.% to 10.4 wt.%. Part of the explanation for the differences in ash content after treatment is that in some cases coal volatiles are changed to fixed carbon whereas with other coals, volatiles are lost from the coal. The use of hydrogen in the dechlorination reduced the coal oxygen content from 4.9 - 15.7 wt.% to 1.3 - 3.5 wt.% with a corresponding increase in heating values of the coals. Proximate and ultimate analyses for the raw and processed coals are listed in Table 2.

VI. Bench-Scale Batch Reactor Production of Desulfurized Coals for Combustion Tests

A. Coals

Selected coals for combustion tests were: PSOC 276, Pittsburgh coal from Harrison County, Ohio; PSOC 282, Illinois #6 from Jefferson County, Illinois; and PSOC 230, Rosebud coal from Rosebud County, Montana. Two of the coals PSOC 276 and 282 are bituminous coals and PSOC 230 is a subbituminous coal. Extensive coal desulfurization data have been obtained on PSOC 276 and 282 coals in phases II and III (ref. 2,3), which was a primary reason for selecting these coals for combustion tests. PSOC 276 coal has a total sulfur content of 3.87 wt.%. PSOC 282 coal has a total sulfur content of 2.2 wt.% in the unwashed, run-of-mine state and 1.54 wt.% in the washed coal. PSOC 230 coal which was first processed in phase III has a much lower total sulfur content of 0.87 wt.% with about two thirds of the sulfur present as organic sulfur.

Two hundred pounds each of PSOC 276, washed PSOC 282 and PSOC 230 coals were ground and classified by Corosil Corp., Corona, California to provide -200 mesh coal for test operations.

The test plan called for conducting combustion tests on the raw coal ground to -200 mesh, followed by tests on the chlorinolysis processed coal (with dechlorination at 400°C) and chlorinolysis processed coal combined with hydrodesulfurization. Thirty pounds each of the raw coals PSOC 276, 282 and 230 were shipped to Penn State for combustion tests at the start of the program. The coal sulfur forms data are listed in Table 1 and proximate and ultimate analyses in Table 2.

The remaining six samples of desulfurized coals for combustion tests were obtained by the bench-scale batch reactor production of the chlorinolysis and chlorinolysis-hydrodesulfurized coals. Laboratory-scale tests were first conducted to select chlorination and hydrodesulfurization conditions for the production of the test coals.

B. Chlorinolysis-Processed Coal

1. Chlorination

PSOC 276, 282 and 230 coals were treated by the chlorinolysis process to provide samples of coal for combustion tests by Penn State. The batch processing data are included in runs 14-22, Table 1. Chlorinations of all the coals for combustion testing were accomplished under identical conditions in the bench-scale batch reactor. Chlorinations were conducted with three kilograms of coal, 4.5 kilograms of water at atmospheric pressure, 20-50°C, 60 minutes reaction time and chlorine to sulfur values of 82% of stoichiometric. Stoichiometric values of Cl_2/S are approximately 8 by weight. The coal slurry after chlorination was filtered under 20-30 inches of vacuum and spray washed twice with water/coal of 2 for each wash.

Recoveries of coal from the chlorination and filtration-wash process were approximately 98-100% for PSOC 276 and PSOC 282 coals and somewhat less, 90-98% for PSOC 230 coal. An exact coal accounting was not obtained. This

would require an ash, chlorine and sulfur analyses of the chlorinated coal at this stage of coal processing in addition to the dry weight of coal recovered. The reduced recovery of PSOC 230 coal relative to PSOC 276 and 282 may be attributed to a higher percentage of coal fines in PSOC 230 coal which were lost in the filtrate. The filtrate from the PSOC 230 coal was refiltered over filter paper in a gooch crucible in order to obtain some added coal recovery. Improvements in grinding of the PSOC 230 coal should reduce the extent of coal fines and the attendant losses of coal in the filtrate.

2. Dechlorination

The coal samples representing the chlorinolysis processed coal were dechlorinated in the bench-scale dechlorinator. Approximately 2 to 3 kilograms of coal were dechlorinated in any one batch with a nitrogen purge of 10 SCFH at 10-20 p.s.i.g., 400°C, 60 minutes and 3-4 RPM rotation of the coal container. A 325 mesh stainless steel screen with a pad of glasswool provided containment of the coal within the coal canister and separate from the downstream trap and discharge piping in most cases. Recoveries of coal in the dechlorinator were: PSOC 276 - 73%, PSOC 282 - 81%, and PSOC 230 - 80%. The losses are attributed in part to mechanical losses of coal, oils and tars and low molecular weight hydrocarbon gases. A trap following the coal container provided a collection of water, oils, tars and coal particles. The exit gases consisted of hydrogen, HCl and coal volatiles as low molecular weight gases. The gases were scrubbed by a 10% Na₂CO₃ solution before being vented to the atmosphere. The amount of chlorinolysis processed coal produced was: PSOC 276-6629 grams (14.6 lbs), PSOC 282 - 6833 grams (15.1 lbs), PSOC 230 - 6774 grams (14.9 lbs.).

3. Sulfur Forms

The sulfur forms data are listed in Table 1. The total desulfurization values were: PSOC 276 - 66%, PSOC 282 - 56% and PSOC 230 - 29%. No organic sulfur removal was found in any of the three coals. A slight analytical anomaly indicated that both PSOC 282 and 230 coals showed apparent slight increases in organic sulfur. Analytical bias could explain this organic sulfur increase. The low desulfurization for PSOC 230 coal was at variance with phase III data for PSOC 230 coal which showed 47% total sulfur removal. However, the chlorination conditions in phase III were fixed at a Cl₂/S value of 38.74, approximately 6 times greater than the Cl₂/S value of 6.56 in the current work, which can easily explain the differences in desulfurization. The indication is that for low sulfur coals, less than 1-2 wt.% sulfur, a higher than stoichiometric Cl₂/S value may be necessary to achieve maximum desulfurization by chlorination.

4. Proximate-Ultimate Analyses

Proximate and ultimate analyses for the three chlorinolysis processed coals with dechlorination at 400°C indicate relatively high retained values of volatiles. Volatiles were reduced from 38-39 wt.% to 23-34 wt.%, with corresponding increases in fixed carbon from 51-59 wt.% to 56-67 wt.%. PSOC 230 coal showed only a 5% loss in volatiles. Ash values decreased slightly for PSOC 276 and increased slightly for PSOC 282 and 230. Heating values increased slightly for all coals. Hydrogen values decreased slightly from 4.40 - 5.67 wt.% to 3.92-4.14 wt.%. The oxygen content increased for PSOC 276 from 5.87 wt.% to 9.62 wt.% whereas PSOC 282 and 230 coals decreased in oxygen content from 9.92-14.9 wt.% to 5.70-6.53 wt.%. The increase in oxygen for PSOC 276

coal can be attributed to the oxidation reaction by chlorinolysis. However, the decrease in oxygen for PSOC 282 and 230 coals, in the absence of a reducing environment is unexpected. The reduced oxygen may be attributed to a loss of oxygenated functional groups during the dechlorination stage. A reduction in oxygen content is commonplace when dechlorination is practiced with hydrogen in lieu of nitrogen as the purge gas.

C. Chlorinolysis-Hydrodesulfurized Coals

1. Chlorination

Laboratory-scale screening studies with PSOC 276 coals indicated that low Cl_2/S values of 2 and 4 provided substantially lower coal hydrodesulfurization than a Cl_2/S value of 8 (stoichiometric). An earlier hypothesis that partial chlorination in conjunction with hydrodesulfurization would be equally effective in coal desulfurization to that achieved with higher chlorine flow rates appears not to be true, at least with PSOC 276 coal. Therefore, the conditions for chlorination that were adopted were identical to those used in producing the chlorinolysis processed coal (without hydrodesulfurization). Chlorinations were conducted at atmospheric pressure, 20-50°C, 60 minutes reaction time and chlorine to sulfur values of 82% of stoichiometric. Chlorination conditions are summarized, runs 23-33, Table 1. Three to four batch reactor runs of 3 kilograms coal per batch were required for each coal to produce the required amount of processed coal for the combustion tests. Coal from the individual runs was blended for the combustion tests. Sulfur forms, proximate and ultimate analyses were performed by the Colorado School of Mines Research Institute (CSMRI) on a blended sample for each coal and are reported in Tables 1 and 2.

Coal recoveries after chlorination and filtration-wash for PSOC 276, 282 and 230 coals parallel the coal recoveries found in runs 14-22 for these same coals Table 1. An exact coal accounting would require sulfur, chlorine and ash analyses of the chlorinated coal. However, without making these corrections, the coal recoveries listed in table 1 are: PSOC 276, 107-110%; PSOC 282, 98-100%; and PSOC 230 90-92%. The higher than 100% recovery for PSOC 276 is attributed to the high weight of chlorine addition to the coal which more than equals the weight loss of ash and sulfur.

2. Hydrodesulfurization

The laboratory-scale screening studies of hydrodesulfurization, Tables 1 and 2, indicated that substantially high reductions of volatiles and hydrogen were obtained by hydrodesulfurization at 700°C. The test data also indicated that Cl_2/S 8 (stoichiometric) was required to achieve high values of coal desulfurization (80-90%), Table 1. The Cl_2/S values of 2 and 4 (25 and 50% of stoichiometric) provided only 62-64% coal desulfurization at 700°C. The use of hydrogen at 100 p.s.i.g. did not appear to provide any advantage over the use of atmospheric pressure hydrogen. Test data (runs 9-11) of three bituminous coals (Pgh. #8 from Greene County, PA.; Ill. #6, from Jackson County, Ill.; Lagle #5 from Moffat County, Colo.) hydrodesulfurized at 500°C showed relatively low coal desulfurization (39-62%), comparable to that obtained from chlorinolysis without hydrodesulfurization.

The intent of the laboratory-scale screening experiments on hydrodesulfurization was to find conditions in which a substantially high coal desulfurization was obtained with a limited loss of volatiles and hydrogen. An

assessment of the available test data including that obtained in phase III data (ref. 3) indicated that hydrodesulfurization temperatures should be at least 600°C to achieve 75% desulfurization (run 1, Table 1), and 700°C to achieve 80-90% desulfurization (run 5, Table 1). At 700°C with PSOC 276 coal the volatiles are reduced to 4.2 wt. % and hydrogen to 1.6 wt.% (run 5, Table 2). A compromise hydrodesulfurization temperature was set at 625-650°C for the batch production of chlorinated-hydrodesulfurized coals for the combustion tests. Much lower temperatures were considered to adversely affect the extent of coal desulfurization without providing much of an advantage in preserving volatiles and hydrogen in the hydrodesulfurized coal unless the temperature was dropped below 500°C.

a) PSOC 276 Coal

The chlorinated PSOC 276 coal (runs 23-25, Table 1) was hydrodesulfurized at 650°C, 5-10 p.s.i.g. using 10 SCFH hydrogen over 3 kilograms of coal for 60-120 minutes. Coal recovery from the hydrodesulfurization was 66% for a total production of 6320 grams (14.0 lbs). The blended coal from the three runs had a total sulfur reduction of 86% with 98% pyritic sulfur and 58% organic sulfur reduction. Proximate and ultimate analyses of the processed coal are included in Table 2. Volatiles in the processed coal were reduced from 37 to 6.5 wt. % with a corresponding increase in fixed carbon from 51 to 89 wt.%. Hydrogen was reduced from 5.6 to 2.1 wt. %. Ash was reduced from 11.5 to 8.6 wt.%. Heating values were increased significantly from 12,755 to 13,479 Btu/lb. The residual chlorine in the processed coal was higher than anticipated at 0.5 wt.% considering the fact that Phase III tests on a laboratory- scale reduced chlorine levels to less than 0.1 wt.%.

b) PSOC 282 Coal

The chlorinated coal was hydrodesulfurized at 632-635°C with 10 SCFH hydrogen over 3 kilograms of coal at 50 p.s.i.g. for 90 minutes. The major differences between the treatment of PSOC 276 and 282 coals was the slight reduction in temperatures, 650 to 635°C, the increase in hydrogen pressure from 5-10 to 50 p.s.i.g. and the introduction of flights in the coal container to provide a better mix between the incoming hydrogen and the coal. The pressure of the hydrogen was increased to 50 p.s.i.g. in order to reduce the gas velocity and thus reduce the coal fines removed from the coal container. Average coal recovery for PSOC 282 coal was the same as PSOC 276 coal at 66% with a production of 5888 grams (12.97 lbs). Total desulfurization was 85% based on the raw unwashed coal sulfur content of 2.2 wt.% and 79% based on the 1.54 wt.% value for the washed PSOC 282 coal. Pyritic sulfur reduction was 93% and organic sulfur reduction was 37% based on PSOC 282 washed coal sulfur values.

Proximate and ultimate analyses are listed in Table 2 (blended coal from Runs 26, 27, 32). Volatiles have been reduced from 33.8 to 7.57 wt.% with an increase in fixed carbon from 59.5 to 82.3 wt.%. Loss of volatiles resulted in an ash increase from 6.7 to 10.1 wt.%. Heating values were essentially unchanged at 13,100 Btu/lb. Hydrogen content was decreased from 4.8 to 2.1 wt.%. Surprisingly, the residual chlorine value was relatively high at 1.59 wt.%. A possible explanation is that the use of a pressurized system at 50 p.s.i.g. reduced the ability of the purge gas to remove the HCl from the coal. Again, this high residual chlorine value is at variance with the phase III laboratory-scale data.

c) PSOC 230 Coal

The chlorinated coals from runs 29, 30, 31 and 33 were hydrodesulfurized at 625-645°C, 10 SCFH hydrogen, 50 p.s.i.g. and 90 minutes. Coal recoveries were low at an average of 55% for a production from the four runs of 5961 grams (13.13 lbs). The substantial loss of coal was in part due to the observed large carryover of coal fines into the trap.

Total sulfur reduction for the blended coal from the 4 runs was 56% with 98% pyritic sulfur reduction and 0% organic sulfur reduction. The relatively low hydrodesulfurization obtained was in sharp contrast to the 75-79% total sulfur reduction found in phase III tests (ref. 3) at 700°C. An apparent explanation is that the reduced hydrodesulfurization temperature of 625-645°C was in part responsible for the lower desulfurization. Another explanation is that the chlorination practiced in phase III (ref. 3) was at a substantially higher chlorine value that provided both a higher desulfurization from chlorinolysis and from the hydrodesulfurization. The combination of the two factors could easily explain the diminished desulfurization for PSOC 230 coal relative to that found in phase III tests.

Proximate and ultimate analyses are included in Table 2 for the blended coal from runs 29, 30, 31, 33. Volatiles have been reduced from 38.9 to 6.25 wt. % with an increase in fixed carbon from 52.1 to 81.8 wt.%. Loss in volatiles resulted in an increase in ash content from 9.0 to 12.0 wt.%. However, the sharp reduction in oxygen from 14.9 to 2.82 wt.% resulted in a coal heating value increase from 11,892 to 12,524 Btu/lb. Hydrogen was reduced from 4.4 to 2.1 wt.%. Similar to PSOC 276 and 282 coals, the residual chlorine (0.49 wt.%) was higher than expected from earlier work. Again, the possibility is that a reduction in pressure would increase the purge gas efficiency in scrubbing out the residual HCl.

VII. REFERENCES

1. Kalvinskas, John J., et al, Final Report for Phase I - Coal Desulfurization by Low Temperature Chlorinolysis, JPL Publication 78-8, November 23, 1977.
2. Kalvinskas, John J., et al, Final Report - Coal Desulfurization by Low Temperature Chlorinolysis, Phase II, JPL Publication 80-15, January 15, 1980.
3. Kalvinskas, John J., et al, Final Report - Coal Desulfurization by Low Temperature Chlorinolysis, Phase III, JPL Publication 81-82, March 1, 1981.

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APPENDIX

**The Pennsylvania State University
Plane Flame Furnace Combustion Tests on JPL-Desulfurized Coal**

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ABSTRACT

The program objective was to reliably determine, under the well-defined and well-controlled simulated boiler combustion conditions generated by The Pennsylvania State University Fuels and Combustion Laboratory plane flame furnace, the combustion characteristics of: (a) three raw bituminous (PSOC-282 and 276) and subbituminous (PSOC-230) coals; (b) the raw coals partially-desulfurized (ca.-60%) by "JPL-chlorinolysis"; and (c) the "chlorinated" coals more completely desulfurized (ca.-75%) by "JPL-hydrodesulfurization," in order to establish to what extent the combustion characteristics of the untreated coals were altered upon JPL-sulfur removal.

The plane flame furnace was preheated to 900°C and fired at 10^4 Btu/hr and at +20% excess air. Residence times of 1-2 seconds, peak flame temperatures of 1400-1500°K, and heating rates of 10^4 K/sec, typical of utility boilers, were simulated.

Upon decreasing the parent coal volatile matter generically by 80% (from 36.6 to 6.8%) and the sulfur by 75% via the JPL desulfurization process, ignition time was delayed 70-fold, burning velocity was retarded 1.5-fold, and burnout time was prolonged 1.4-fold. Total flame residence time increased 2.3-fold.

The JPL desulfurization process appears to show significant promise for producing technologically combustible and clean-burning (low-SO₂) fuels.

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Contract Objective

The purpose of the research program, entitled, "Plane Flame Furnace Combustion Tests on JPL-Desulfurized Coals," was to reliably determine, under well-defined and well-controlled simulated boiler combustion conditions, the combustion performance characteristics (ignition times, burning velocities, and burnout times) of three (3) samples of raw (as received) bituminous (PSOC-282 and 276) and subbituminous (PSOC-230) ranks of coal, three (3) samples of the same raw coals partially desulfurized (ca.-60%) by a Jet Propulsion Laboratory (JPL) "chlorinolysis" process, and three (3) samples of these "chlorinated" coals more completely desulfurized (ca.-75%) by a more severe JPL-patented "hydrodesulfurization" process, in order to establish to what extent the burning characteristics of the untreated coals were altered upon sulfur removal.

Plane Flame Furnace: Description

Figures 1, 2, 3, and 4 schematically illustrate components and the general design of the furnace that has been extensively used at The Pennsylvania State University Fuels and Combustion Laboratory for studies of combustion on pulverized fuel flames. This furnace was designed to give safe operation for pulverized coal premixed with cold air to produce a plane flame, that is, a residence time distribution corresponding to close to plug flow with no back-mixing into the flame. Essentially, the furnace consists of a pulverized fuel-air premixer and burner, a down-fired vertical combustion chamber, and an uprising refractory leg connected to a steel stack.

The premixer-burner is situated on the top of the combustion chamber. It receives the mixture of fuel plus primary conveying air, mixes it thoroughly with the secondary air, and disperses the mixture in a plug flow manner. The shape of the premixer-burner is a truncated pyramid of square cross-section whose base is fitted into a two row bank of water-cooled copper tubes. The pyramid expands downwards with an angle 10.6° between the center line and its sides. The dimensions of the base resting on the top of the water-cooled tubes are 6.5" x 6.5". The pyramid is constructed of stainless steel plates which are bonded together with high temperature air-setting mortar (Franset, J. H. France Co.). The pyramid is easily removable for inspection of the interior of the furnace.

The water tube bank consists of two rows of horizontal tubes. The tubes in each row are one outside tube diameter apart and rows are separated vertically by about one inch. The top of each tube is fitted with a stationary vane of triangular cross-section that tapers from base width equal to the outer diameter of the tube to a sharp peak located about one inch above the center line. The vanes prevent the accumulation of pulverized fuel dust on the top of the tubes and direct the flow of fuel particles through the bank with minimum turbulence. The two rows of tubes are staggered in such a fashion that the empty spaces between the tubes in a row are in exact vertical alignment with the tubes of the other row. This arrangement makes the tube bank function as an efficient radiation shield, yet still allows the fuel particles to pass through. The water-cooled tube bank forces the flame to stabilize at the desired position and it prevents the flame from flashing back into the premixing zone. The tubes are of 1/4" thick copper wall while the vanes are constructed of 24 gauge galvanized sheet soft silver soldered onto the tubes.

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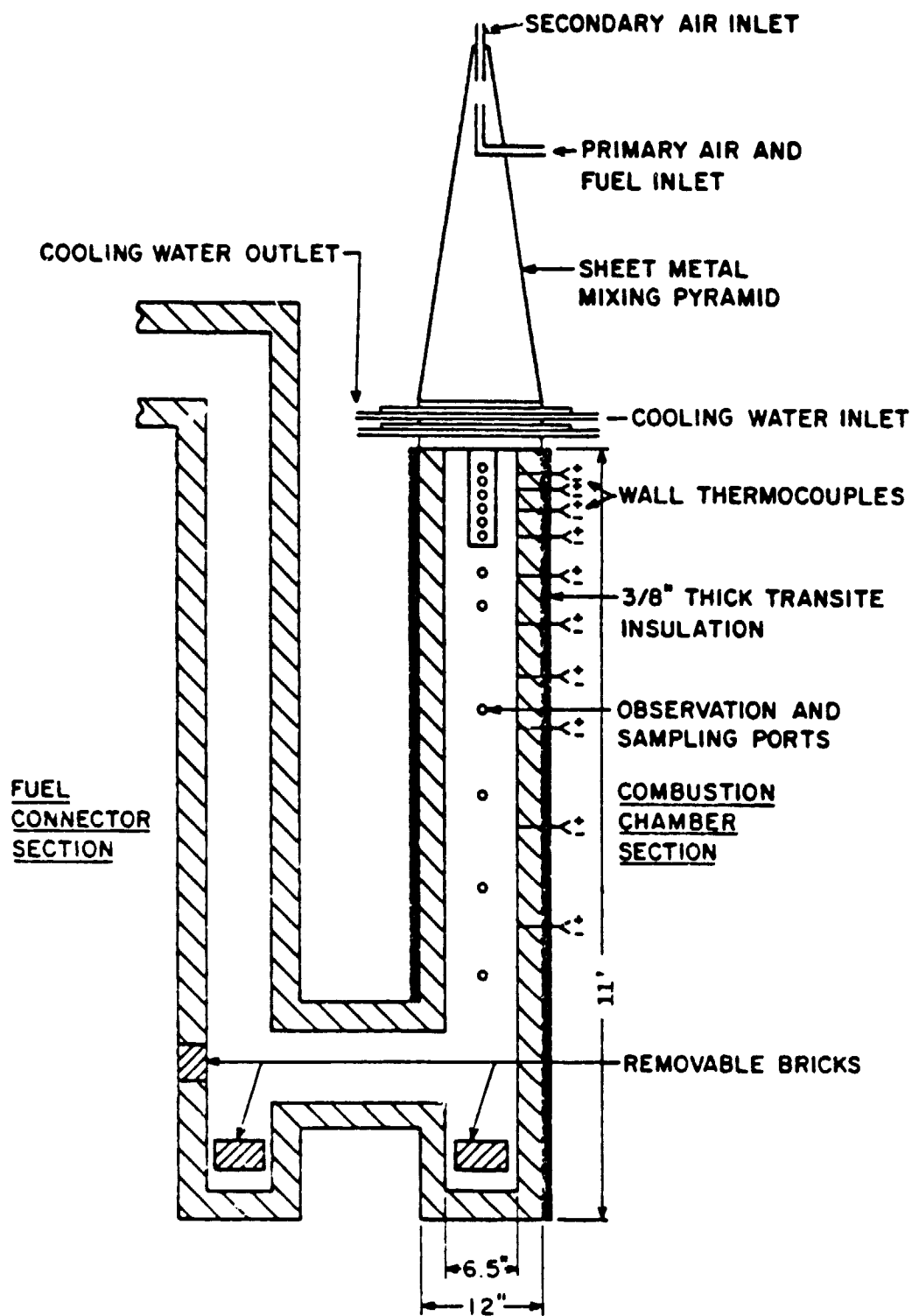


Figure 1. Plane Flame Furnace Schematic

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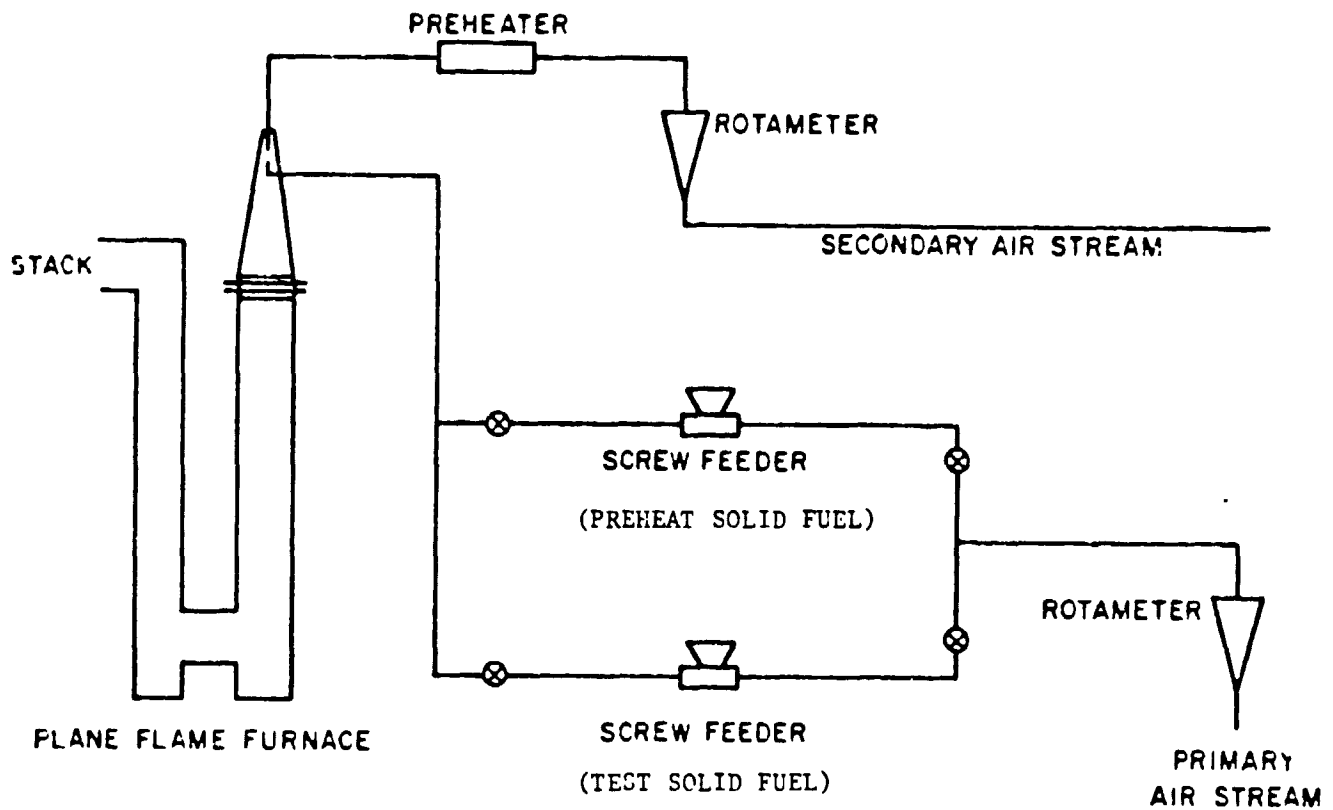


Figure 2. Diagram of Plane Flame Furnace Feeder System

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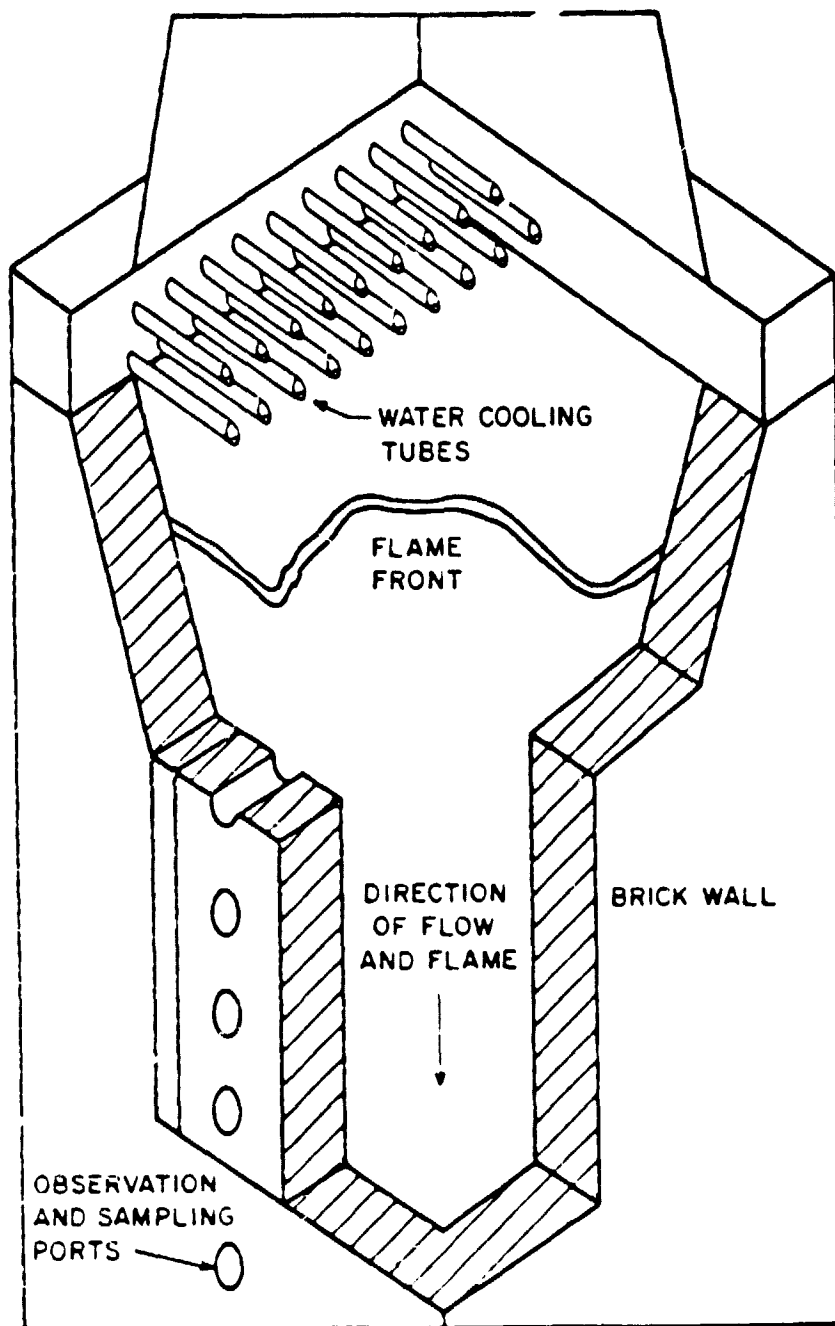


Figure 3. Section Showing Water-Cooled Flame Stabilizer

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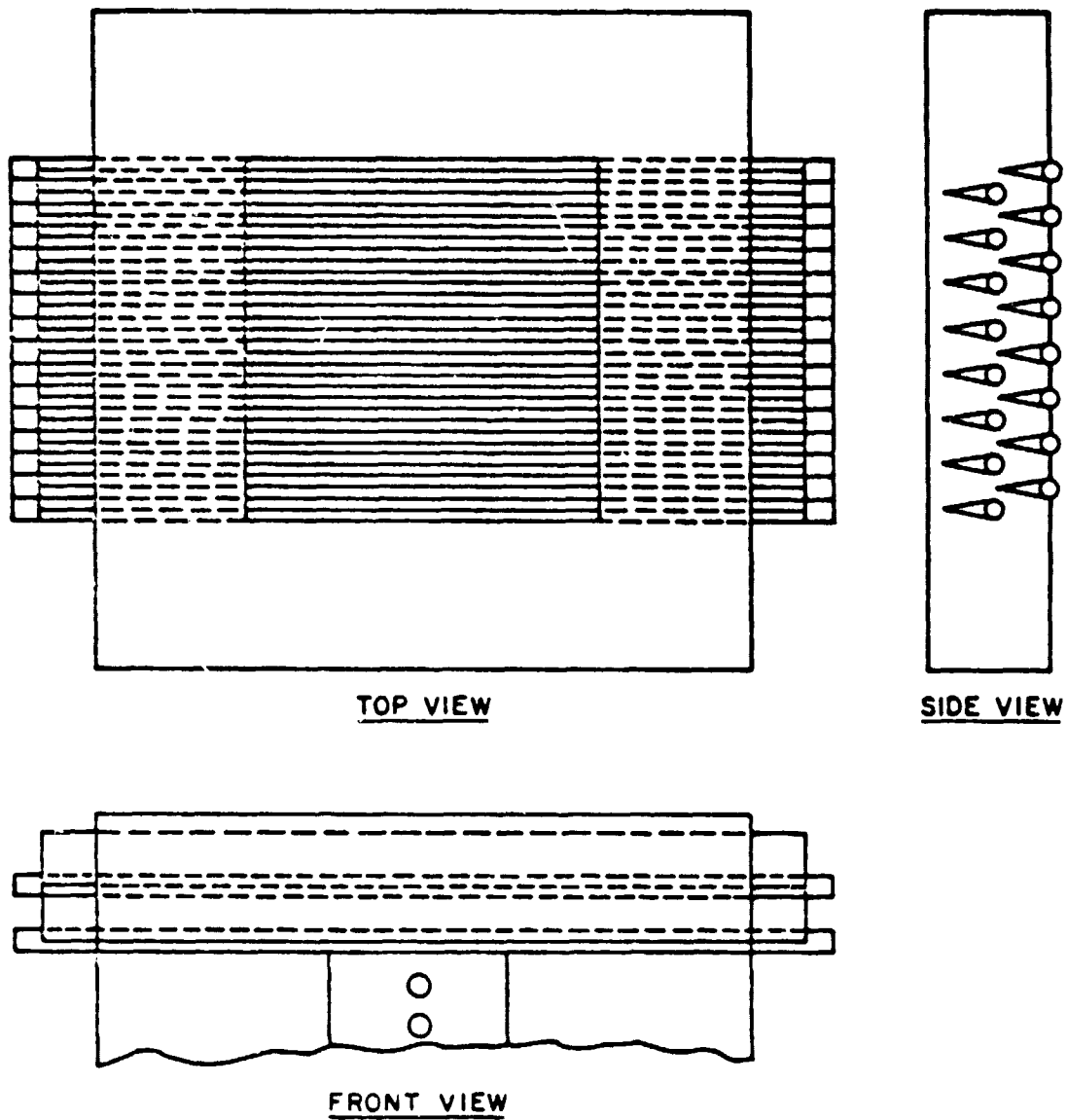


Figure 4. Detail of Cooling Water Tubes

Water flow is commenced before the furnace is fired, obviously, and maintained at the end of a test until the furnace is cool, to prevent melting of the silver solder.

The combustion chamber consists of four vertical walls constructed of insulating refractory bricks, bonded together with high temperature mortar. The bricks are composed of 50% alumina and 50% silica, and can withstand up to 1530°C temperature. The height of the vertical combustion chamber is approximately 335 cm, interior cross-section area is 6.5" square (16.51 cm), and the thickness of the walls is 5" (12.7 cm). The height of the combustion chamber was recently increased from 226 cm to 335 cm to achieve longer particle residence time, and the wall thickness was increased from 6.35 to 12.7 cm to reduce heat loss. The combustion chamber is encased with 3/8" thick transite sheet to reduce heat loss and eliminate air leakage.

All but one of the sampling ports on the front side wall of the furnace are kept closed during the furnace operation using ceramic plugs. The junction between the uprising flue and the combustion chamber is located at a short distance above the bottom of the chamber in order to collect product material at the base. The flue is constructed of the same type of bricks and mortar as used for the combustion chamber, but are a single layer thick (6.35 cm).

The air supply system consists of a primary air line and a secondary air line. The primary air line supplies compressed air (80 psi) for the pulverized fuel ejector (see later) and the secondary air line supplies low pressure air, produced by a blower with a capacity of 350 SCFM. A 2" gate valve in the secondary air line controls the flow of air. The primary and secondary air lines are connected to two rotameters (Schulte and Koerting Co., 0-25 SCFM, 0-30 SCFM), respectively. The total flow rate of combustion air is controlled by adjusting the required total flow through both primary and secondary air lines.

The pulverized fuel feeder system consists of a large primary hopper, a small secondary hopper, a vibratory feeder, and a venturi ejector for introducing the fuel into the primary air, which is then pneumatically carried to the premixer-burner. The venturi device is composed of a funnel whose spout is fitted into the throat of a asymmetric venturi. The funnel is made out of brass and the venturi is made by cutting and sealing a notch in a 3/8" stainless steel respectively of 60° and 12° to the axis of the tube, and to a depth of about 2/3 of the diameter of the tube. The funnel is soldered into an opening left in the throat of the venturi. With the unit installed in the primary air line, the flow through the venturi creates a suction at the spout of the funnel which is sufficient to allow pulverized fuel to be pulled from the funnel into the air line by atmospheric pressure.

Figures 5 and 6 show the details of the feeder. It consists primarily of a commercially-obtained SCR-20 Vibra-Screw Feeder. The maximum deviation in feed rate from the mean value during a given run is typically only ±5%.

Before the start of a test, the steel stack is heated with a gas burner located at the base to create natural draft conditions (30-45 minutes). During this time, the feeder is calibrated by collecting test fuel over timed periods and weighing it.

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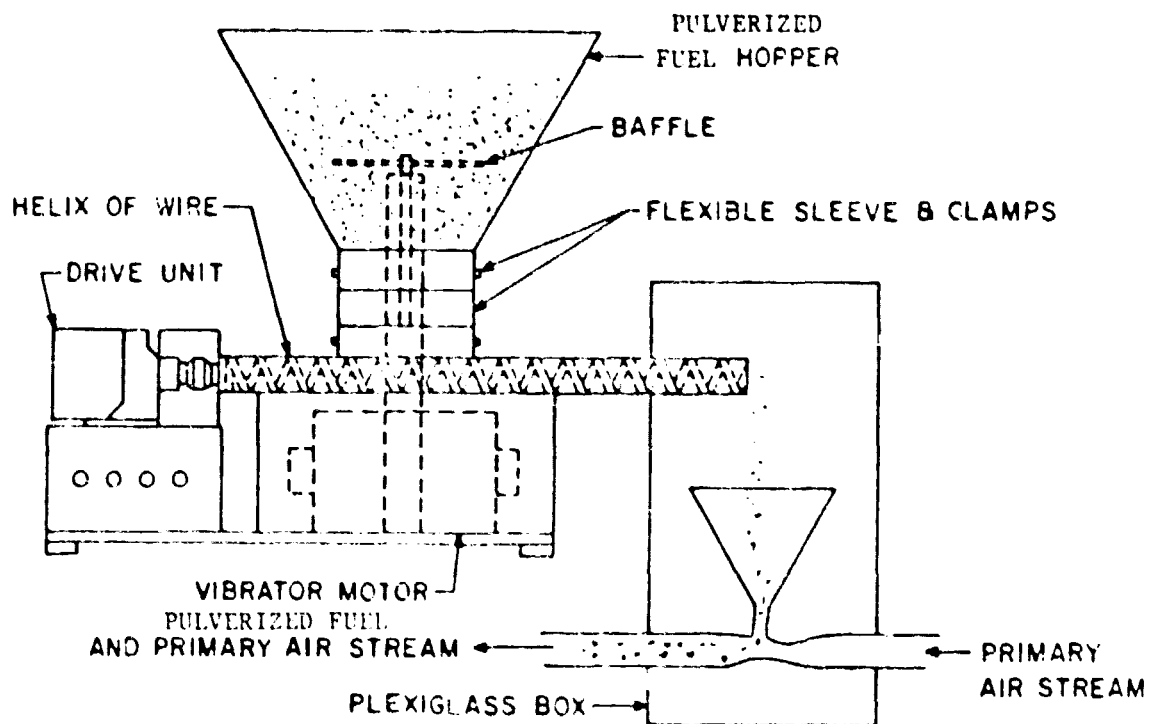


Figure 5. Diagram of Vibrating Screwfeeder System

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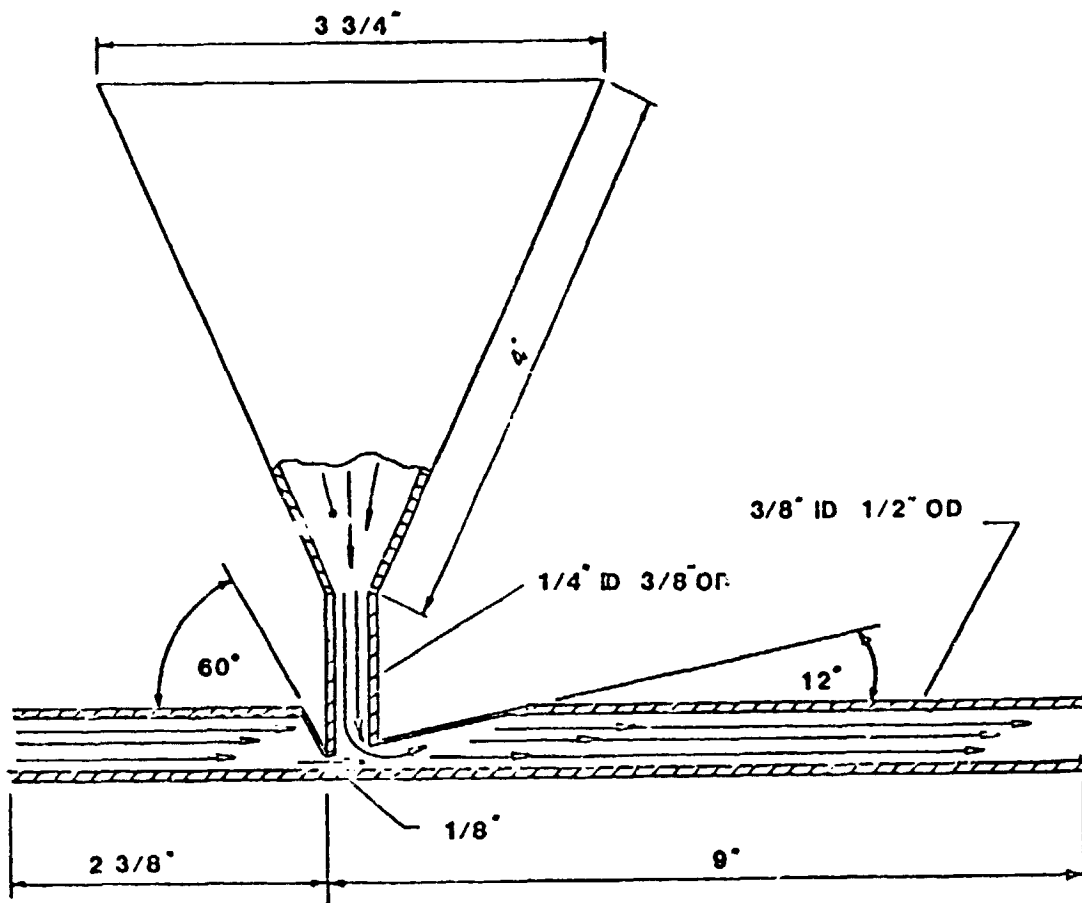


Figure 6. Details of Ejector

The furnace is raised in temperature before the start of firing with coal by means of a water-cooled gas burner (see Figure 7) inserted in the top of the furnace below the tube bank. A small gas flame is used initially, with a low air flow through the tube bank, and as the furnace enclosure becomes hotter, more gas and air are supplied at a rate less than flame failure, until full burner capacity is reached. More will be said about the ignition procedure required for determining fuel ignition temperature later.

The following precautions were considered important for safe and correct furnace operation:

1. The pulverized fuel feed rate must be recalibrated for each type of fuel used.
2. The funnel attached to the venturi should be checked periodically, since blockage of the nozzle can occur because of larger fuel particles or foreign material.
3. Before the furnace is fired, water must be passing through the water tube banks.
4. The furnace wall temperature must be checked periodically to confirm the presence of the flame.
5. Material must be removed every 30 minutes from the bottom of the furnace and stack, in order to prevent pressure build-up in the furnace.
6. Before any actual test is conducted, steady state temperature must be obtained.
7. After the experiments are finished, the air and feeder lines must be first turned off. The water, however, must run through the water tube banks for the following night so that the furnace may cool down without damage to the mixer-burner.
8. The high pressure gas line must be turned off at the main.

Plane Flame Furnace Diagnostics: Description

The measurement of wall and gas temperatures, and the collection of gas and solid samples require the construction of special purpose probes, which has been done. The designs are shown schematically and discussed briefly.

Wall Temperatures: Thermocouples

In order to measure the furnace inner-wall temperatures, twelve thermocouples are connected to a 24-point Esterline Angus (Model E1124E) temperature recorder that scans the twelve thermocouples once every 24 seconds. The thermocouples are fixed along the longitudinal center-line of the right side of the combustion chamber. The positions of the wall thermocouple stations are shown in Figure 1. The thermocouple wire (0.128" diameter Pt/Pt-10% Rh) is insulated with alumina double-bore tubing (.0126" O.D. x 0.0233" I.D. x 6" long) and

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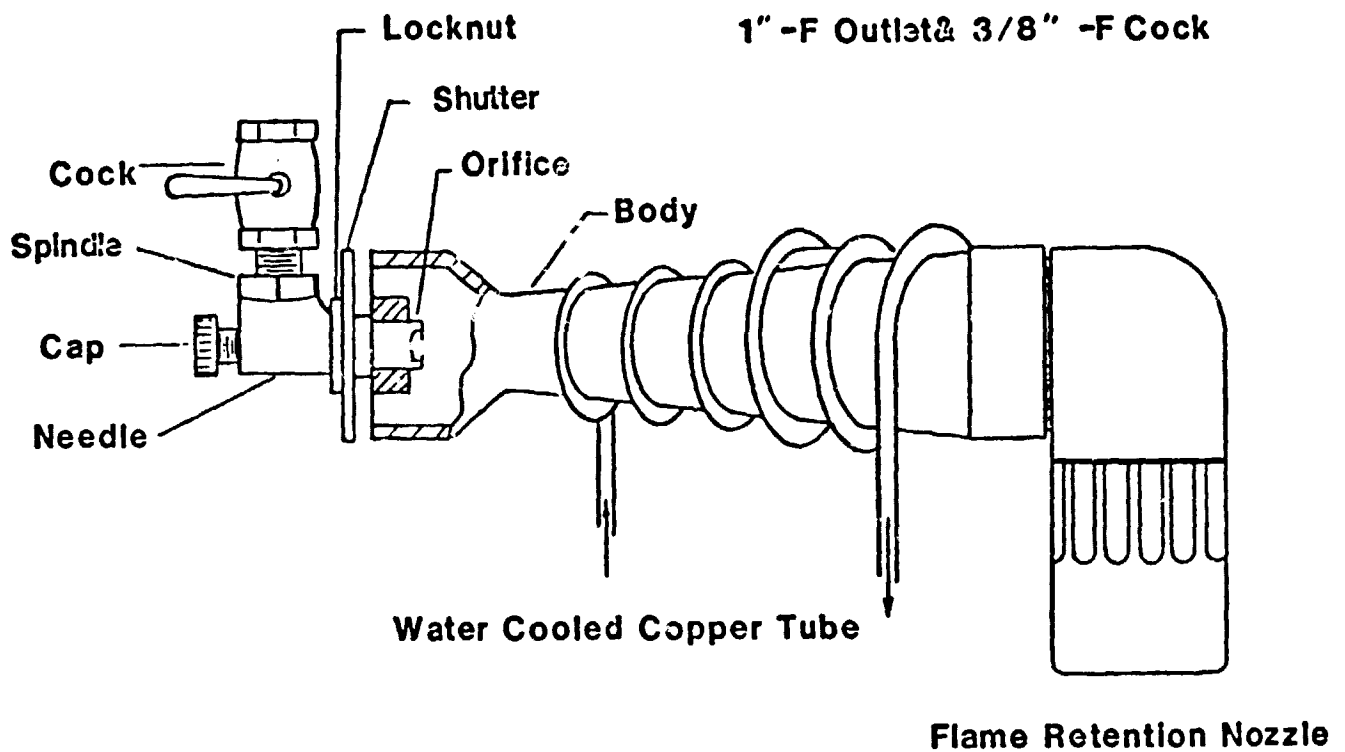


Figure 7. Gas Burner

installed in an alumina protecting tube (0.218" O.D. x 0.150" I.D. x 6" long) with one end closed.

Gas Temperatures: Suction Pyrometer

Furnace gas temperatures are measured with a water-cooled suction pyrometer, with which flue gas is pulled at high velocity over a shielded thermocouple, as shown in Figure 8. It consists of a Pt/Pt-10% Rh thermocouple that is placed into a two-bore ceramic tube. The head of this tube is protected by another ceramic tube (O.D. 19"/64, I.D. 13"/64 and 8" long) with one end closed. This whole assembly is covered by an open-ended ceramic shield tube and gas is withdrawn through the annulus. This head is supported on a water-cooled body composed of two concentric copper tubes through which water is circulated to cool the hot gases after they have passed the thermocouple head. The suction pump has a capacity of 0.2 CFM.

Wall-Gas-Temperature Correlation

Figure 9 shows how axial furnace wall temperatures, as measured with thermocouples, compare with gas temperatures, as measured with the suction pyrometer.

Gaseous combustion Products: Gas Sampling Probe

The probe used for collecting gas samples from a pulverized-fuel flame must meet the following basic requirements: (a) it has to be sufficiently cooled to protect the probe from thermal destruction and to quench the sample rapidly; (b) it has to be small enough that its presence does not significantly affect the flow conditions of the flame; (c) it has to be completely sealed to prevent leakage of air into the sampling system or furnace; and (d) it has to be capable of separating the gaseous sample from the solid material. The gas sampling probe used for the JPL desulfurized coal combustion tests is shown in Figure 10. The probe is water-cooled, and the sample enters through a nozzle that is directed upstream, parallel to the flow. It turns a 90 degree bend and then travels through a 0.2 inch inner diameter copper tube to the filter chamber where the solid material is completely removed. The sample is collected by inserting a standard gas collection bulb in line just downstream from the exit of the probe. Heat transfer is very good in the small diameter tube, thus, the gas sample is very rapidly cooled. The filter chamber, that uses a small filter-paper disc (0.625 inch) supported by a wire screen, is easily taken apart for cleaning.

Gaseous products of combustion sampled at various distances down the axis of the furnace are analyzed via two techniques: (i) batch, using a gas chromatograph (Carle Series-S-157A Random Access GC), that provides separation of H_2 , O_2 , N_2 , CO , CO_2 , H_2S and 20 various hydrocarbons, or (ii) on-line, using non-dispersive infrared (CO , CO_2) and paramagnetic (O_2) analyzers.

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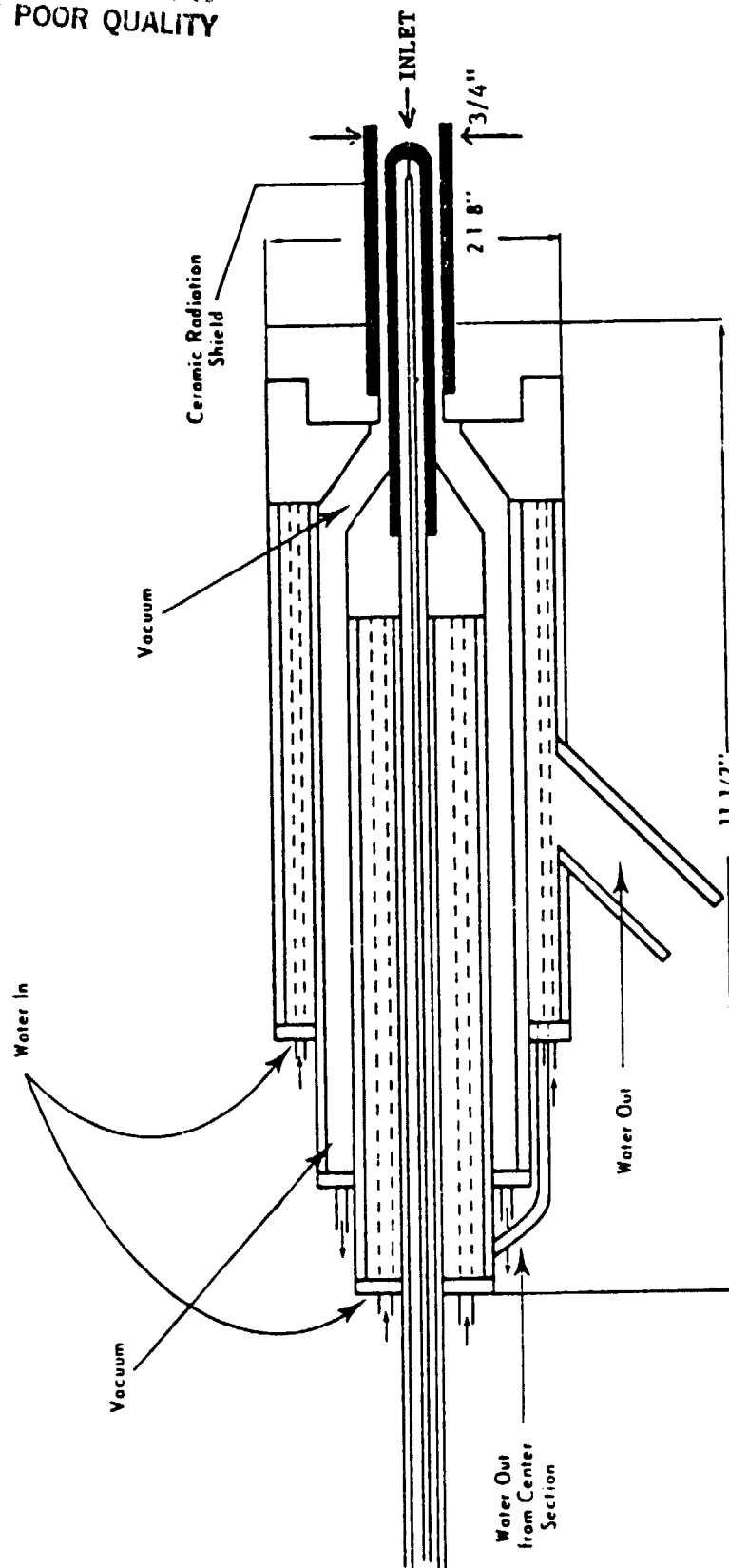


Figure 8. Single Shield Suction Pyrometer for Flame Temperature

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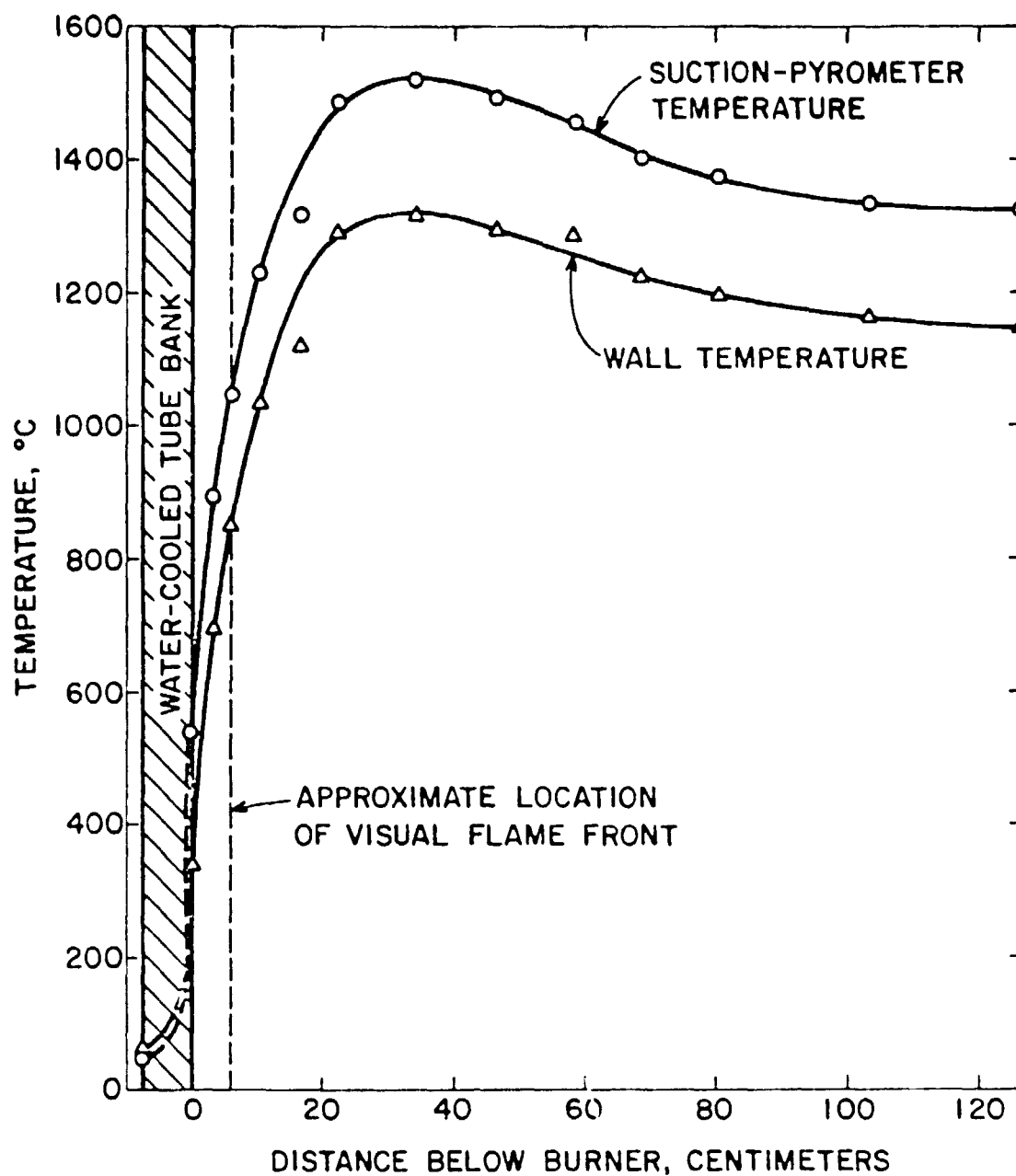


Figure 9. Temperature Profiles in the Plane Flame Furnace

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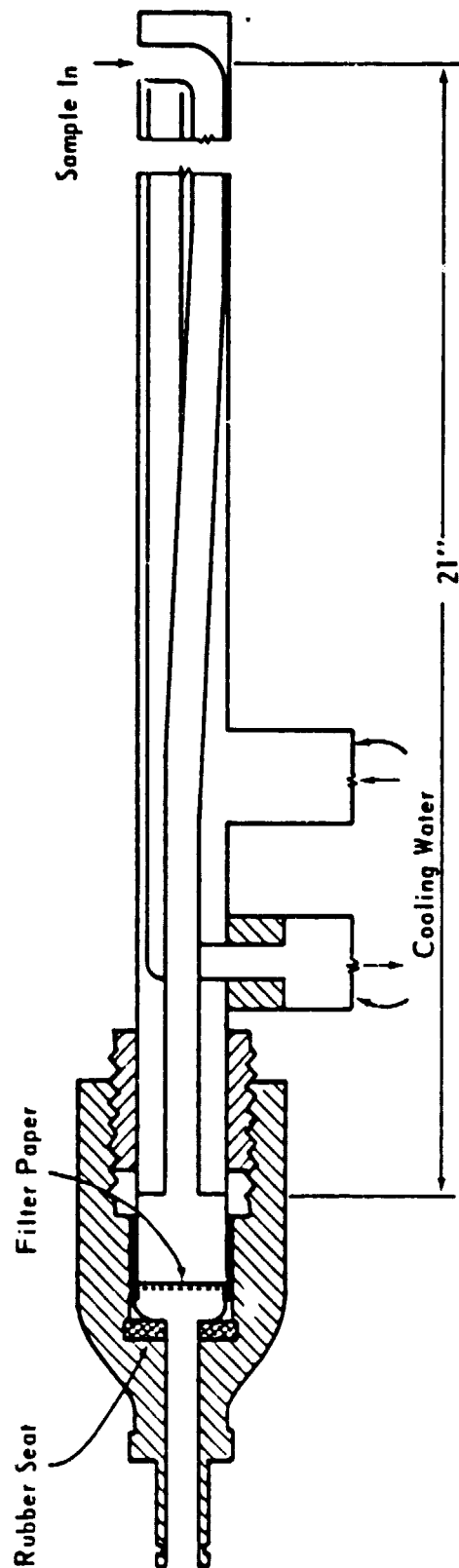


Figure 10. Gas-Sampling Probe

Solid Combustion Products: Solid-Sampling Probe

In addition to being able to collect a solid sample that is representative of the material in the flame and to quench it at a sufficiently rapid rate, solid-sampling probes for use in flame research are subject to two requirements that prove to be very significant: (i) the probe must be large enough to contain both the water-cooling supply pipes and the facilities for collecting and handling the solid material, but, at the same time, (ii) the probe must be small so that its presence in the furnace has no significant influence on the flow conditions in the flame.

The standard procedure in the past was to construct the probe large enough to contain a filter chamber in the end that actually went into the flame. In such a probe, a suction line leads from outside the furnace to the filter chamber; another tube leads from the filter chamber to a nozzle that opens into the flame; a water jacket surrounds the whole system. When suction is applied to the end of the probe located outside the flame, hot material enters the nozzle and travels through the filter chamber where the solid material is collected. Heat is transferred from the sample to the cold walls of the tube leading to the filter chamber. This standard design necessitates an outer diameter of at least two inches and is, therefore, not practical in the present investigation; its use would obviously violate the second requirement mentioned above, namely, the presence of a cold, two-inch diameter probe would certainly exert a significant influence on the conditions in a flame that is only several inches thick itself.

In order to use a small diameter probe, a design was required in which the filter chamber is located outside the flame. The only parts of the probe that penetrate the flame are the nozzle through which the particles enter, the tube that leads from the nozzle to the filter chamber, and an appropriate water-cooled jacket. The lower limit for the size of this design was determined by the first requirement mentioned above, namely, sufficient space must be available in the probe to accommodate both the water-cooling features and the facilities for collecting and handling the solid sample. The facilities for water-cooling are themselves subject to a serious lower limit in size because a certain minimum flow rate of cooling water is necessary to prevent thermal destruction of the probe and to insure adequate cooling of the sample. The size of the facilities for collecting and handling the solid material in the probe are also subject to a lower limit because of the following points that were learned by experience in the preliminary experiments. In the region of flames of pulverized bituminous coal that roughly corresponds to that of most rapid devolatilization, the particles become very sticky and tend to cling to the inside surface of the cold tube through which they are being transported; this tendency to stick to the tube promotes clogging and eventually leads to blockage of the passageway. The ability to resist clogging is inversely related to both the inside diameter of the sampling tube and the velocity with which the material is drawn through the tube. Therefore, in order to transport a sample of material from a point in the "sticky" zone of the flame to a filter chamber located outside the furnace, a probe must be used in which the diameter of the tube carrying the sample is above a certain lower limit. At the same time, the sampling tube must be below a certain upper limit because, with a given sampling velocity and probe temperature, the rate of cooling of the sample is inversely related to the inside diameter of the sampling tube.

After designing and testing several different models, each of which contributed something to the required knowledge about the critical dimensions and behavior of the probes, a design was finally attained which satisfied the above mentioned requirements (see Figure 11). The essence of this design is its ability to remove a sample from the flame, quench it rapidly, separate the solid from the gaseous material, and collect the solids for further study, all with only a small, 5/8 inch portion of the probe inside the flame. This probe is composed of three individual units, each of which is water-cooled, and which are easily disconnected to permit a thorough cleaning after the collection of each sample. The probe is of the suction type, with the sample being drawn through a filter chamber where the solid material is collected on a filter paper, the area of which is relatively large to avoid a large flow resistance. The filter paper used (Glass Fiber Type E - 2 in. diameter; Gelman Instrument Company) was designed to trap all particles greater than 3 microns, which at the same time permitted a large flow rate of gas through the unit. However, once the filter cake begins to form, particles as small as a fraction of a micron are trapped.

The nozzle is designed to offer the selection of a 90 degree entrance or a "straight-through" entrance, the particular entrance desired being chosen by eliminating its alternate with a brass plug. This feature was incorporated into the design at a time when clogging by sticky particles was thought to be promoted by forcing them to execute a 90 degree turn upon entering the probe. However, experimental tests disproved this hypothesis, and the preferred 90 degree entrance was used exclusively in collecting samples in the principal data runs. The 90 degree nozzle is preferable because it allows the entrance into the probe to be directed upwards when the probe is positioned horizontally. Since this is the same direction (but of opposite sign) as the movement of the particles in the flame, the particles can enter the probe without changing their direction until they are already inside the nozzle. With a correct suction velocity (which had to be determined in this investigation) such a nozzle is capable of collecting samples which are true representatives of the material in the flame.

The passageway through which the sample first flows is a standard 0.5 inch copper tube (0.315 in. I.D.). From the point of view of rapid quenching of the sample, a smaller tube would be more desirable; however, probes equipped with smaller tubes were designed, built, and thoroughly tested in preliminary experiments which showed that diameters smaller than the one finally used were not practical for use in this experiment because of blockage by sticky particles.

The second, longer section of the probe was designed to be able to permit particles to cling to the cold walls, without succumbing to blockage of the passageway or a significantly decreased rate of cooling. The cooling surfaces of this long annulus collect a very significant portion of the sample when probing the sticky region of the flame. This section of the probe finishes the cooling process which occurs mainly in the first section.

The size of the portion of the probe actually penetrating the flame (5/8 inches in diameter) is perhaps not as small as would be desired ideally for avoiding a significant effect on the conditions in the flame; but here again, this particular size was used out of necessity, since a significantly smaller tube would not contain both the tube through which the sample flows and the

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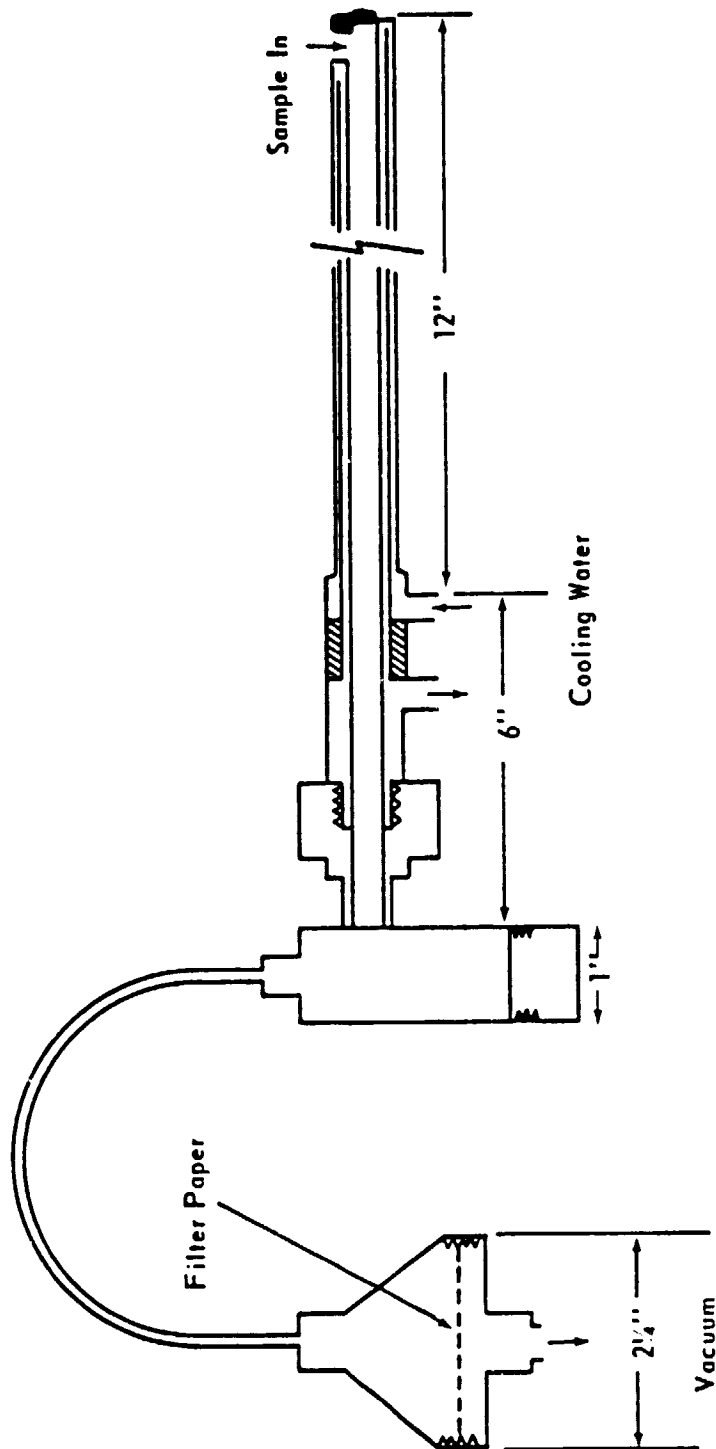


Figure 11. Solid-Sampling Probe

inlet and outlet passageways for cooling water. However, this size was regarded as suitable with respect to not affecting the flame since, in a special experiment, it was found that no significant change occurs in the temperature of the inside surface of the combustion chamber at a given point when the probe is injected into the center of the flame at the same location.

Combustion Data Acquisition

The plane flame furnace was fired at 8-10 pounds of pulverized JPL coal per hour and at +20% excess air. In order to better simulate the pulverized coal characteristics used in typical electric utility power boilers, for which the JPL-desulfurized coals is ultimately intended, the JPL-supplied coals were pulverized to a mass mean particle diameter of 75 microns. This procedure also permits any necessary comparisons to be made between the JPL coals and other solid fuels test-burned using the PSU-FCL plane flame furnace.

Flame and wall temperatures and compositions of gaseous and solid products of combustion were characterized as a function of residence time (axial distance down the furnace centerline) by sampling the combustion environment through ports distributed along the vertical axis of the furnace (see Figure 1). Residence time was calculated as a function of downward distance with the use of the coal/air cold volumetric flow rate, the square-cross-sectional area of the combustion chamber, and the flame temperature profile. The volumetric flow rate (cm^3/sec) divided by the cross-sectional area (cm^2) yields a flow velocity (cm/sec). The ratio of the flame to the ambient temperature times the input cold flow velocity yields the flame speed (cm/sec). The downward integrated position or flame thickness (cm) divided by the flame speed (cm/sec) at that point yields the elapsed residence time from time zero to that position (sec). Once the furnace has been calibrated in terms of residence time, then ignition times, burning velocities, and burnout times were determined as a function JPL-coal sample. These data indicate how well JPL-desulfurized coals will perform as boiler fuels on a comparative basis.

The progress of combustion in a pulverized coal flame is best monitored by measuring the appearance of carbon dioxide products and/or the disappearance of elemental carbon in the fuel, and thus following "carbon burnoff." Carbon burnoff can be measured in two independent ways: (a) on a gas-phase product of combustion basis (CO_2) from fuel ultimate analysis information and (b) on a solid-phase product of combustion basis (elemental carbon in the char) from fuel ultimate analysis information. From the coal's ultimate analysis, one can readily calculate [2] the identities and quantities of gaseous products of combustion at 100% carbon conversion and at any stoichiometry. The percent CO_2 in the exhaust gases at complete combustion and at +20% excess air was calculated for each JPL-coal. The ratio of the experimentally measured CO_2 flame concentration and this absolute CO_2 maximum concentration at any downward vertical position within the furnace yields the extent of combustion up to that particular residence time. These data can be independently checked by collecting a solid sample and measuring its elemental-carbon content. By comparing this information with the elemental-carbon content in the unburned-coal's ultimate analysis, one can again measure the progress of carbon burnout as a function of residence time. In this calculation, it must be assumed that all the elemental carbon is converted to CO_2 . Independent measurements have validated this assumption in air-rich (+20% excess air) flames, i.e., there was no

carbon monoxide or hydrocarbons in the exhaust gases and the exhaust O_2 concentration was a constant 3.5%. With these data on carbon burnoff and residence time, important events in the initiation, propagation, and termination of a flame can be defined: ignition time, burnout velocity, and burnout time, respectively. Ignition time is defined as the residence time required for 1% coal carbon burnoff. Burnout time is the time required for 100% carbon burnoff. The burning velocity is the quotient of the distance over which a flame exists (or flame thickness) and the residence time that has transpired over that interval. Burning velocity can be thought of as an overall rate of combustion once a flame has been ignited.

Test Coal Shipments and Analysis

All nine JPL-desulfurized and supplied coals have been test-burned in the plane flame furnace at this time. As per the Statement of Work, ignition times, burning velocities, and burnout times have been determined for each JPL coal sample.

The JPL shipped the test coal samples to the PSU-FCL in three stages. On December 17, 1981, the PSU-FCL received 30 pounds each of the three (3) raw coals, with identities given according to the PSU Coal Research Section Coal Sample and Data Bank, PSOC-282, -276, and -230. On February 5, 1982, the PSU-FCL received 17 pounds each of the JPL-chlorinated (CL) and mildly-desulfurized versions of the aforementioned parent coals. On March 10, 1982, the PSU-FCL received the final shipment of 18 + 1 pounds each of the JPL-chlorinated/hydrodesulfurized (CL/HDS) and severely-desulfurized coals.

The coal characteristics of all nine JPL-test coals are given in Table I. Each has been assigned a test number according to convention at the PSU-FCL. Compositional data on the three raw coals was taken from JPL Publication 81-82 [1]. The compositional data on the JPL-treated coals were communicated to Prof. Reuther in a letter from Dr. Kalvinskas dated April 9, 1982 (JK-dy-TRSE-345-4).

Combustion Test Results on JPL-Coals

Plane Flame Furnace Standard Conditions

Prior to a combustion test on any JPL-desulfurized coal or parent coal, the plane flame furnace was preheated to a set temperature using a standardized ignition procedure. Previously, experiments had been executed to calibrate the plane flame furnace according to its time/temperature preheat history. Figure 12 shows the highest-temperature regions of the plane flame furnace combustor profile as a function of preheat time. Thermocouple stations #10-12, at 30-76 centimeters downward from the water-tube bank, recorded the three highest wall temperatures within the combustor temperature profile when the plane flame furnace was preheated with a natural gas flame; station #11 typically recorded the highest furnace wall temperature. Hence, in order to experimentally set the preheat temperature of the plane flame furnace at, e.g., 500°C, 700°C, or 900°C, the natural gas flame was fired for 0.5, 1.0, or 7.0 hours, respectively. Once the desired preheat temperature was reached, the gas burner was shut off, removed, its entry port plugged, and the desired steady-state pulverized coal feed established. The coal firing rate was set at 10^4 Btu/hour

Table 1. Compositions of Raw and JPL-Desulfurized Coals

| PSU-FCL - Test No. | Coal | JPL Process | Ultimate Analysis | | | | | Proximate Analysis | | | | | Heating Value (Btu/lb) |
|--------------------------|----------|----------------|-------------------|------|------|------|------|--------------------|----------------------------------|-----------------|-----------------|--------|------------------------------|
| | | | C | H | N | S | O | Ash | Volatile Matter (dry, wt%) | Fixed Carbon | Moisture (%) | | |
| | | | | | | | | | | | | | |
| JPL-1 | PSOC-282 | RAW | 74.8 | 4.82 | 1.69 | 1.60 | 9.92 | 6.70 | 33.80 | 59.5 | 3.10 | 13,092 | |
| JPL-2 | PSOC-282 | CL | 77.2 | 3.92 | 1.83 | 0.68 | 5.70 | 7.76 | 25.10 | 67.2 | 0.71 | 13,060 | |
| JPL-3 | PSOC-282 | CL/HDS | 82.0 | 2.13 | 1.75 | 0.32 | 2.12 | 10.10 | 7.57 | 82.3 | 1.18 | 13,167 | |
| JPL-4 | PSOC-276 | RAW | 71.6 | 5.67 | 1.28 | 3.91 | 5.87 | 11.50 | 37.20 | 51.3 | 1.89 | 12,755 | |
| JPL-5 | PSOC-276 | CL | 72.7 | 3.93 | 1.46 | 1.31 | 9.67 | 9.88 | 23.50 | 66.6 | 0.48 | 12,792 | |
| JPL-6 | PSOC-276 | CL/HDS | 84.4 | 2.07 | 1.73 | 0.53 | 2.14 | 8.63 | 6.50 | 84.9 | 0.82 | 13,479 | |
| JPL-7 | PSOC-230 | RAW | 56.6 | 4.40 | 1.06 | 0.87 | 14.9 | 9.03 | 38.90 | 52.1 | 7.26 | 11,892 | |
| JPL-8 | PSOC-230 | CL | 77.1 | 4.14 | 1.11 | 0.62 | 6.53 | 9.79 | 34.20 | 56.0 | 0.61 | 12,127 | |
| JPL-9 | PSOC-320 | CL/HDS | 80.9 | 2.14 | 1.20 | 0.38 | 2.82 | 12.00 | 6.25 | 81.8 | 0.82 | 12,524 | |

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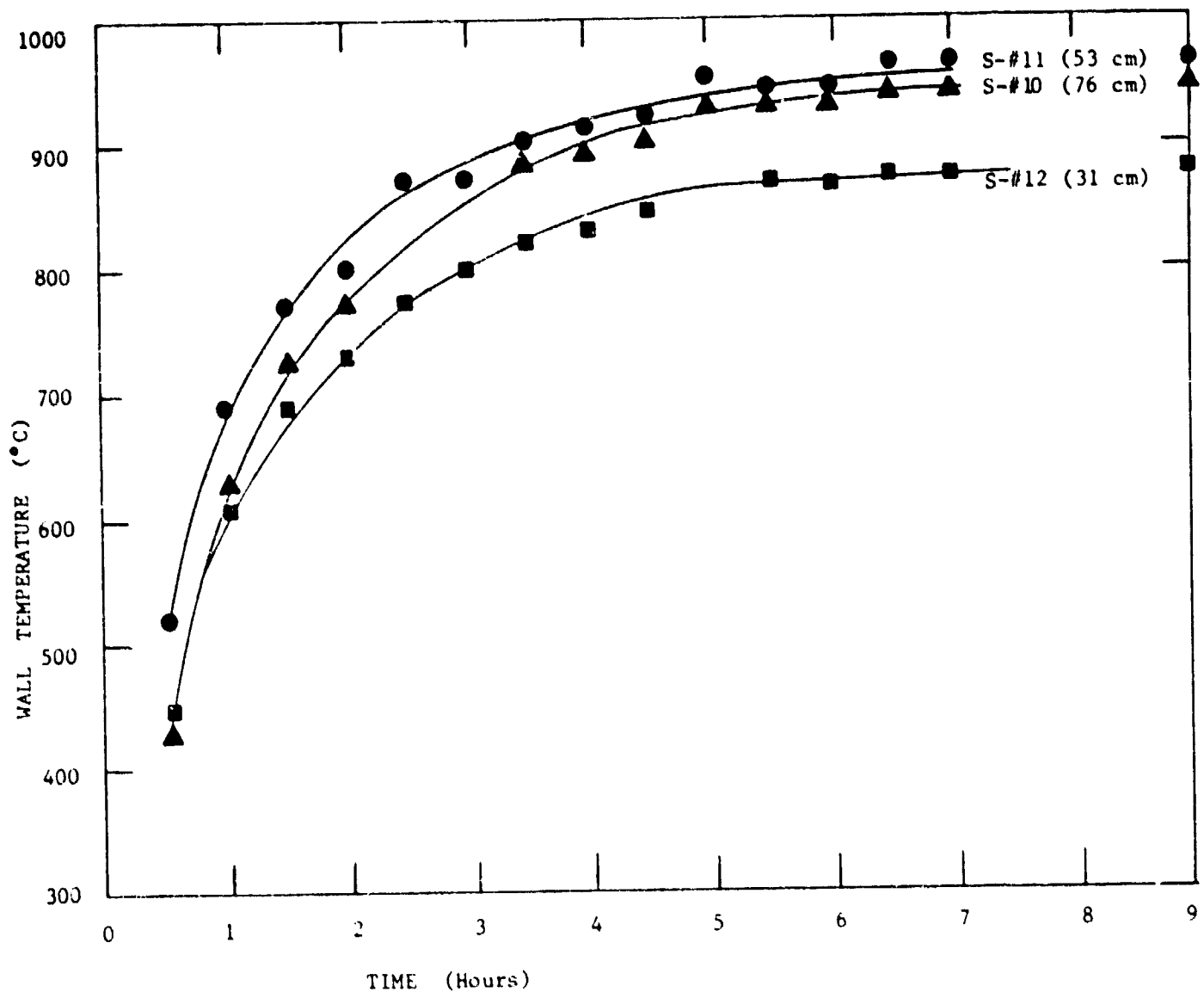


Figure 12. Variation of Maximum Furnace Wall Temperature at Specific Locations Downstream of the Tube Bank as a Function of Time for Natural Gas/Air Flames

corresponding to ca., 7.8 pounds of coal per hour; the coal/air stoichiometry was set at +20% excess air.

For all the combustion tests on JPL-coals reported in this document, furnace preheat was constant at 900°C.

Gas-Phase JPL-Coal Flame Graphical Data

Figures 13-15 graphically present the plane flame furnace exhaust carbon dioxide (CO₂) profiles for each of the three JPL-coal shipments, i.e., sample Nos. JPL-1, 4, 7 (Fig. 13); JPL-2, 5, 8 (Fig. 14), or JPL-3, 6, 9 (Fig. 15). In these figures, each of the 3 raw, chlorinated, or chlorinated/hydrodesulfurized coals are compared with the same process condition (or none) for the three different coals. The CO₂ profile data given in Figs. 13-15 have been reported as a function of residence time. It should be noted that the flame temperature profiles for all three sets of three samples were spatially and quantitatively comparable to each other. Specifically, the wall temperature profiles for all nine JPL-coal flames peaked at a temperature of 1350 + 40°K and at a residence time that was ca. 100 + 25 milliseconds (msec) prior to the residence time at which the maximum in the CO₂ exhaust gas concentration was realized. The flame cooling rates after their respective maxima were also comparable. A succinct way of summarizing and interpreting this JPL-coal flame temperature profile behavior is to state that once ignited, JPL-desulfurization had little or no effect on the maximum temperature of the raw coal and that the delay in reaching these maxima was as one switches from raw-to-chlorinated-to-chlorinated/hydrodesulfurized coal reflects only the difficulty in ignition.

Figures 16-18 present the same plane flame furnace CO₂ profile data as given in Figs. 13-15, but now they are plotted so that the effect of chlorinolysis and chlorinolysis/hydrosulfurization on the (ignition, reaction, and burnout) combustibility of each different raw coal is illustrated. The trends in the results as a coal is desulfurized (and devolatilized) were not unexpected: ignition time is delayed, burning velocity or overall rate of reaction decreased, and burnout time was prolonged. The raw coals, JPL-1, 4, and 7, all exhibited a zero ignition delay time. As each raw coal was desulfurized, with the exception of JPL-8 -- which was not desulfurized and devolatilized to the same extent that its analogues (JPL-2 and 5) were -- the JPL-processed coal derivative exhibited an ignition delay time.

Solid-Phase JPL-Coal Flame Graphical Data

In order to corroborate the gas-phase flame data concerning the progress of combustion, samples of the solid products of combustion (chars and, eventually, ash) were taken as a function of residence time within the furnace. The analytical work done on these samples was performed by The Pennsylvania State University Mineral Constitution Laboratory using a Carlo-Erba Elemental analyzer #1106 for C-H-O-N determinations. Figures 19-21 illustrate the results of JPL-coal flame solid sampling in the same format as that given in Figs. 16-18, i.e., the effect of chlorinolysis and chlorinolysis/hydrodesulfurization on the combustibility of each different raw coal is illustrated.

The solid-phase JPL-coal flame data agreed very well with the gas-phase JPL-coal flame data.

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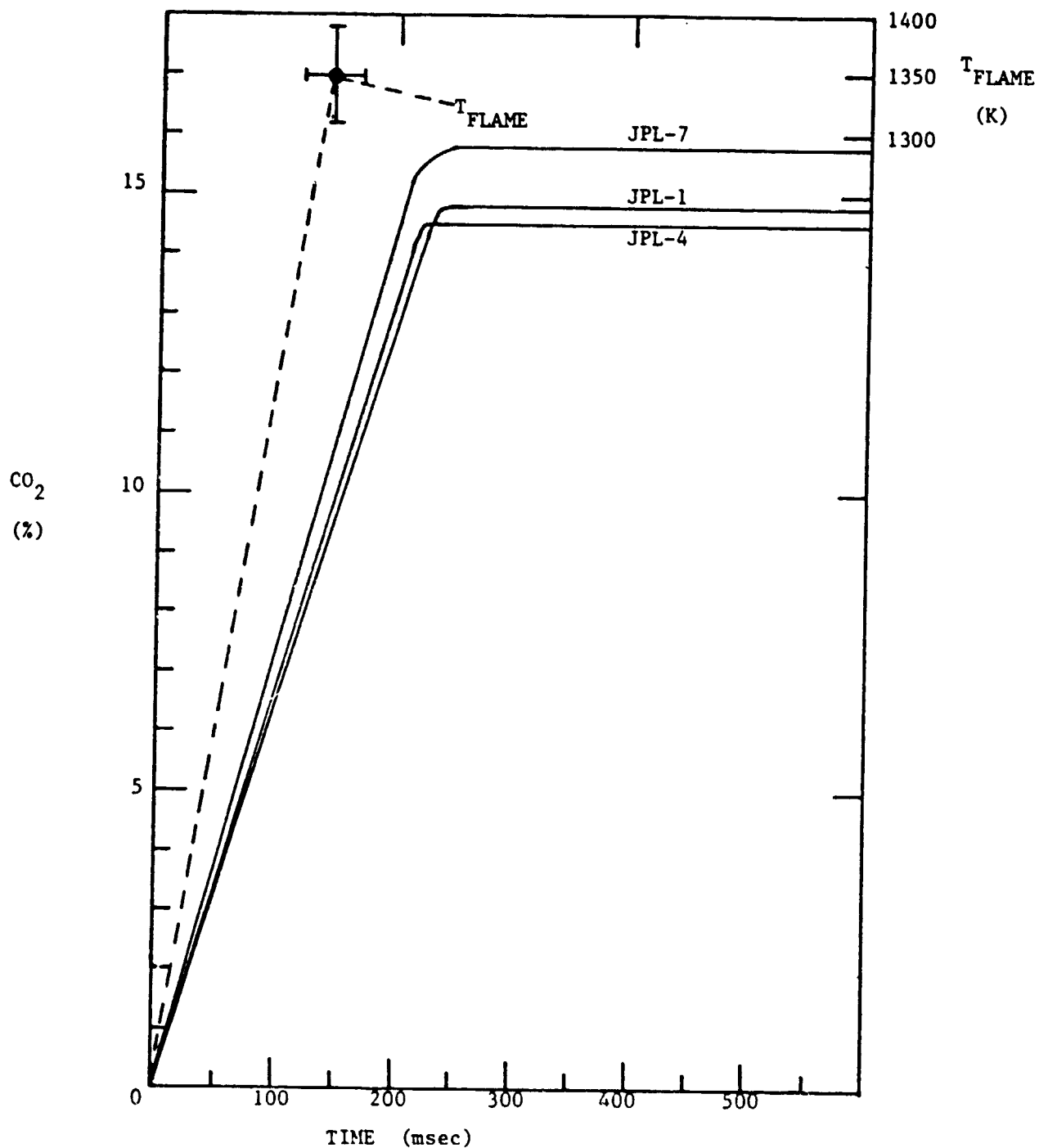


Figure 13. Gas-Phase Combustion Performance Characteristics of Raw JPL-Test Coals: JPL-1, JPL-4, JPL-7

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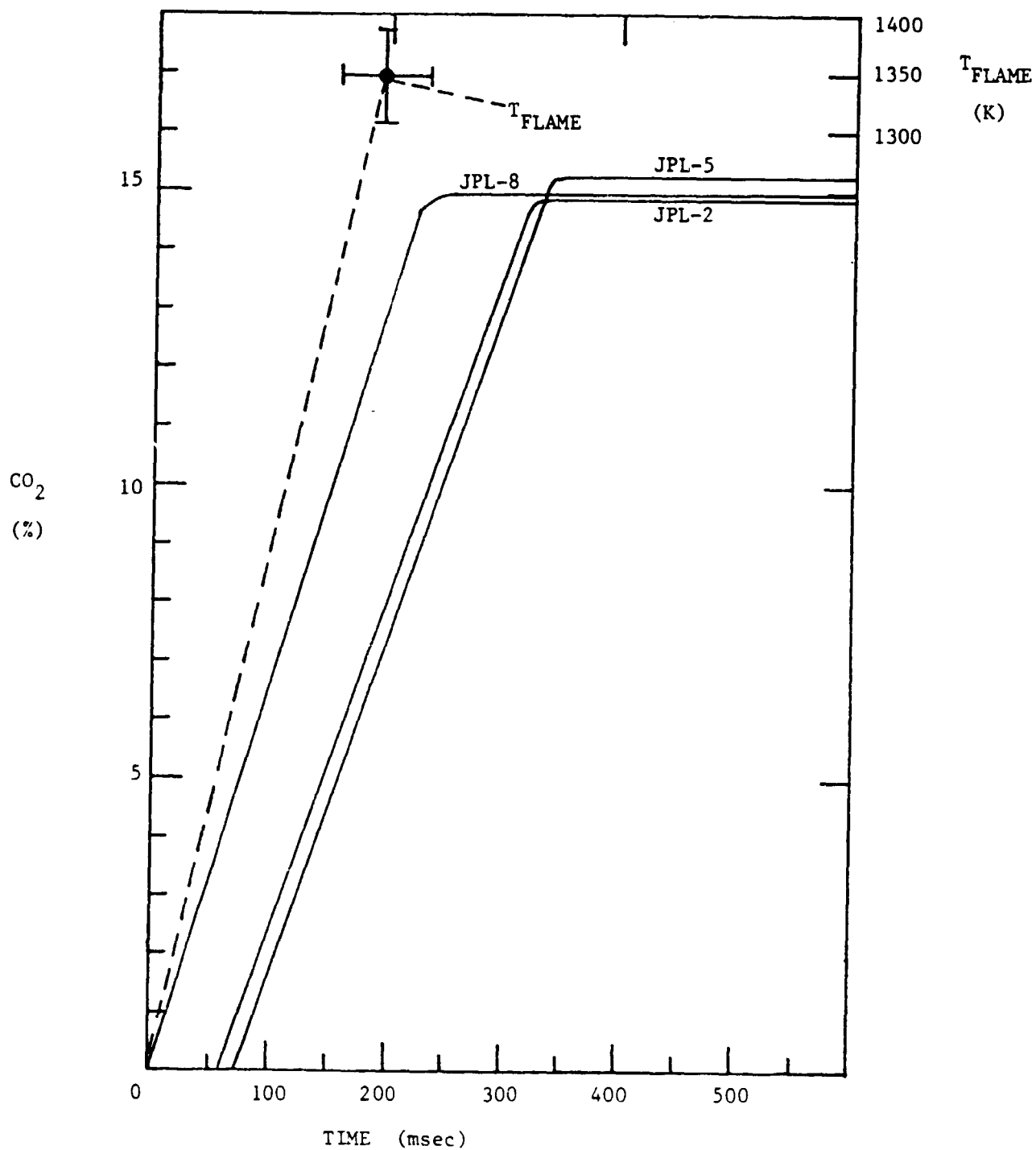


Figure 14. Gas-Phase Combustion Performance Characteristics of Chlorinated JPL-Test Coals: JPL-2, JPL-5, JPL-8

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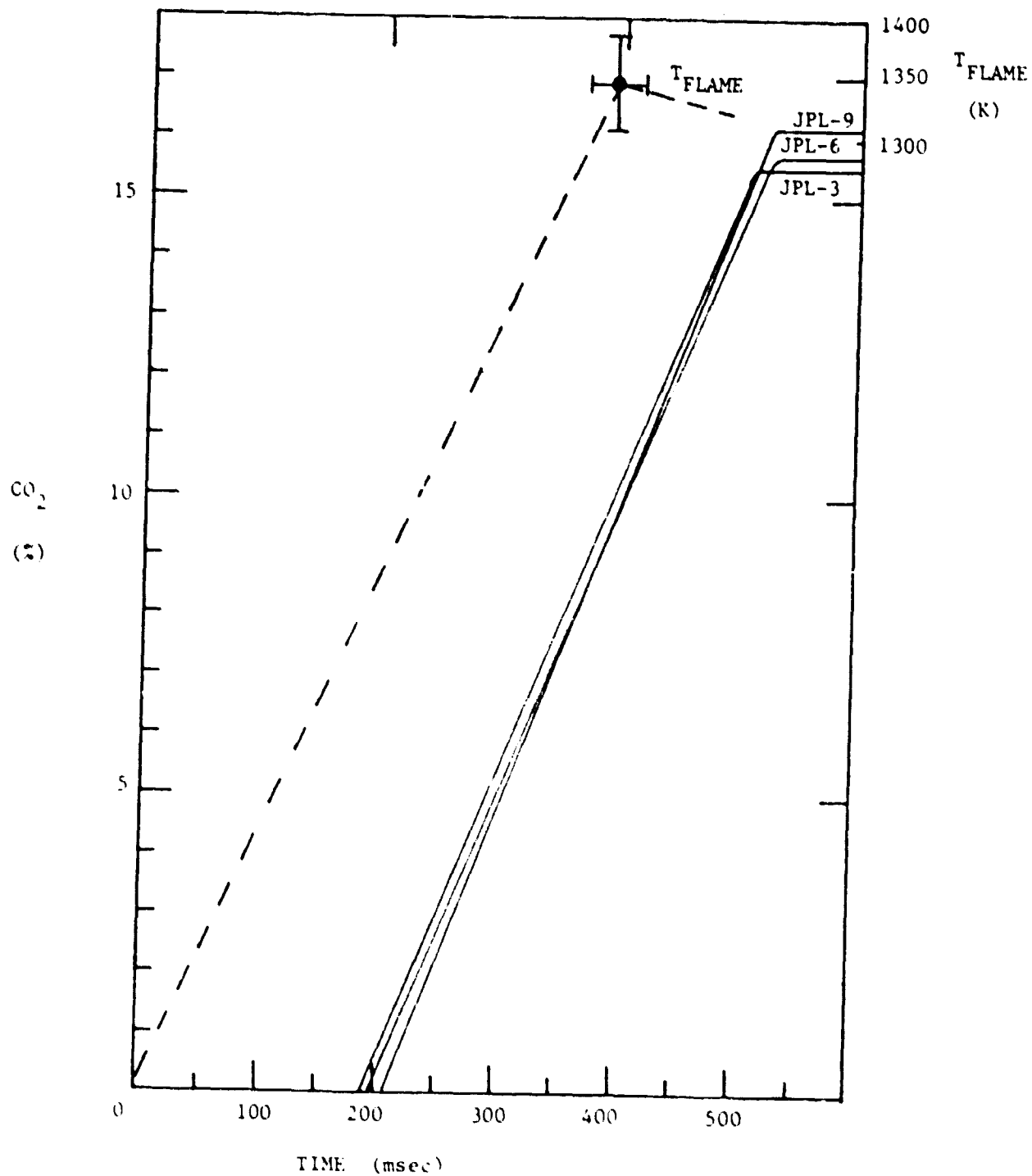


Figure 15. Gas-Phase Combustion Performance Characteristics of Chlorinated/Hydrodesulfurized JPL-Test Coals: JPL-3, JPL-6, JPL-9

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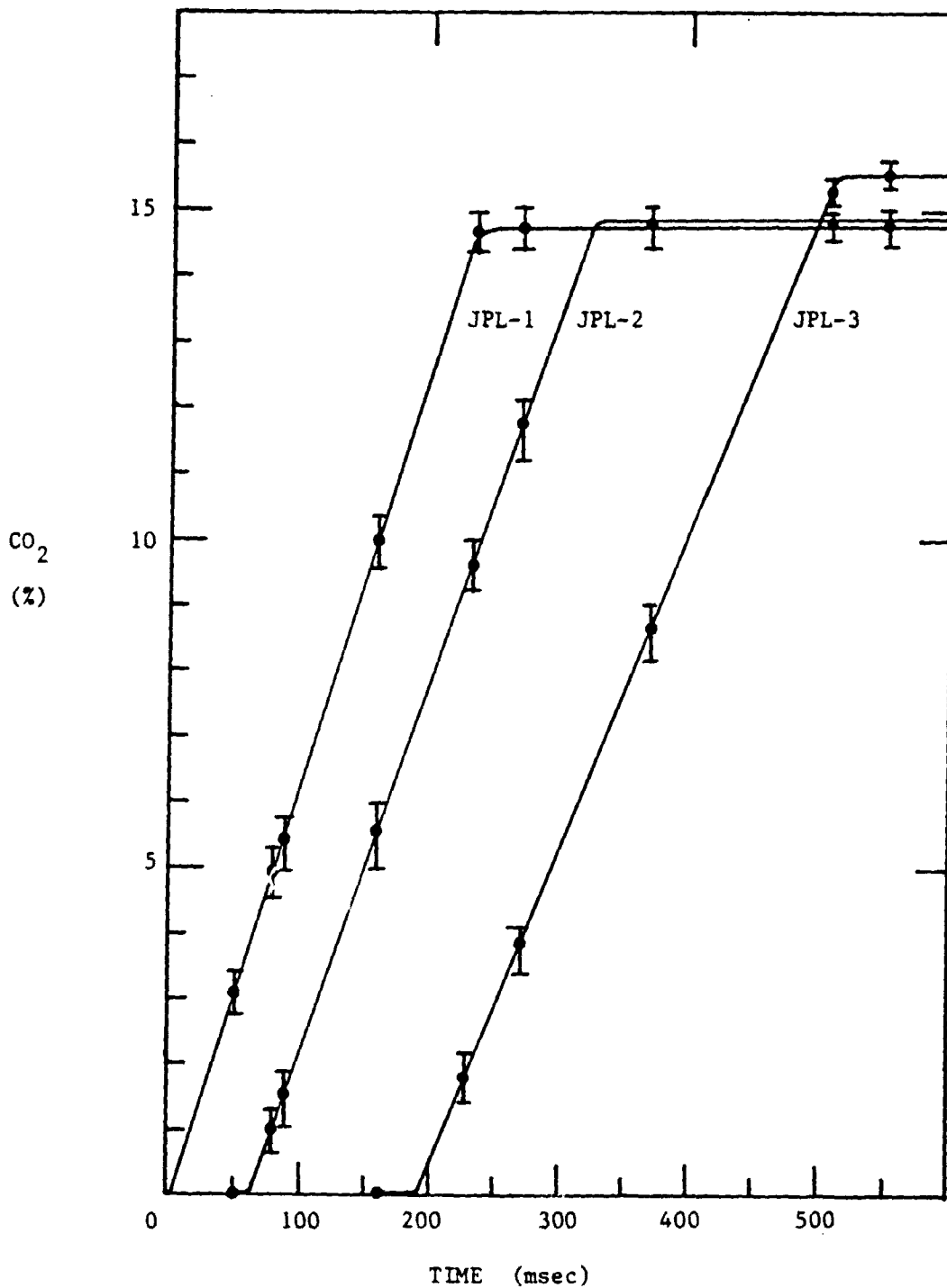


Figure 16. Gas-Phase Combustion Performance Characteristics of Raw and JPL-desulfurized PSOC-282 Coal: JPL-1, JPL-2, JPL-3

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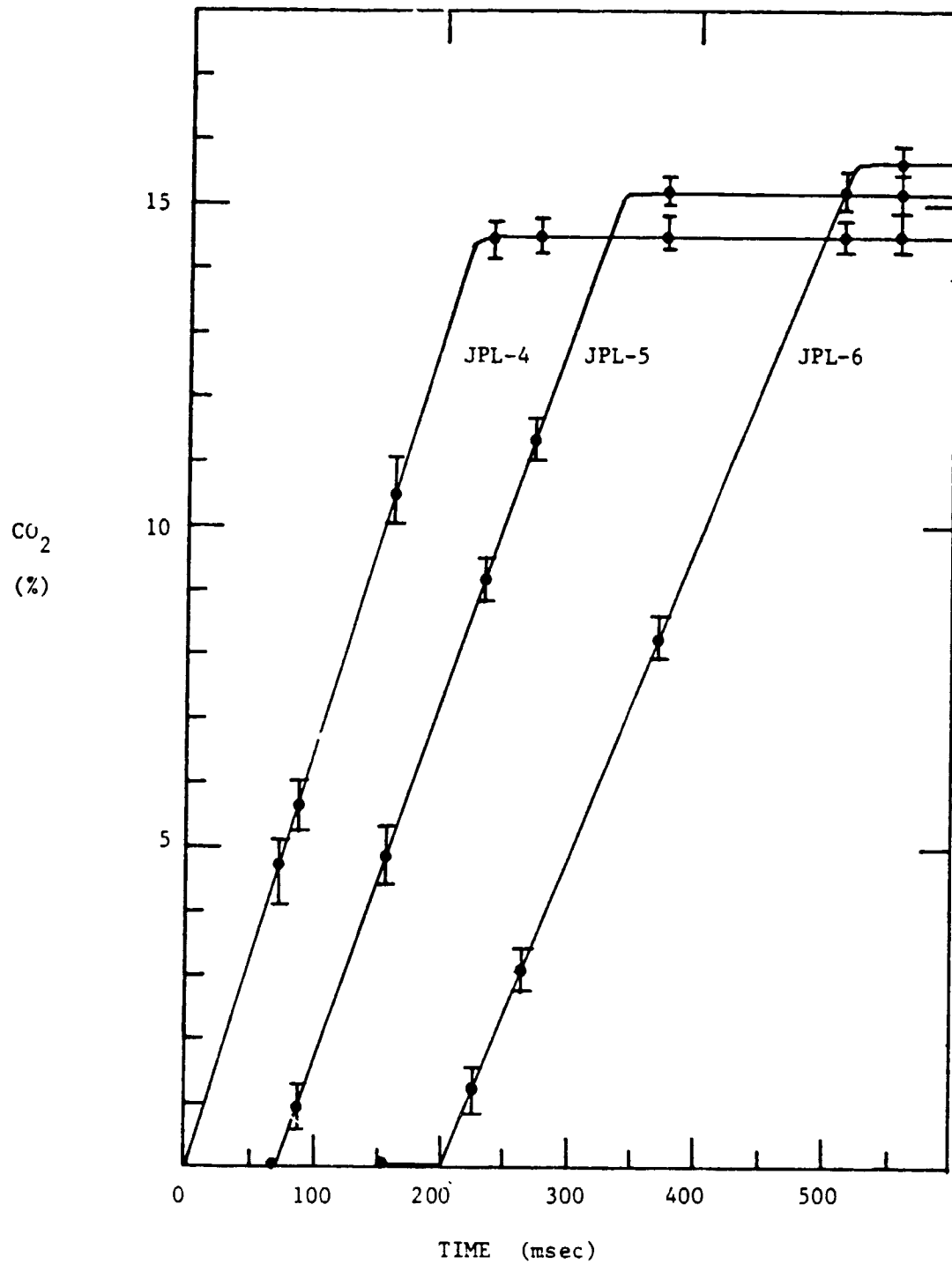


Figure 17. Gas-Phase Combustion Performance Characteristics of Raw and JPL-Desulfurized PSOC 276 Coal: JPL-4, JPL-5, JPL-6

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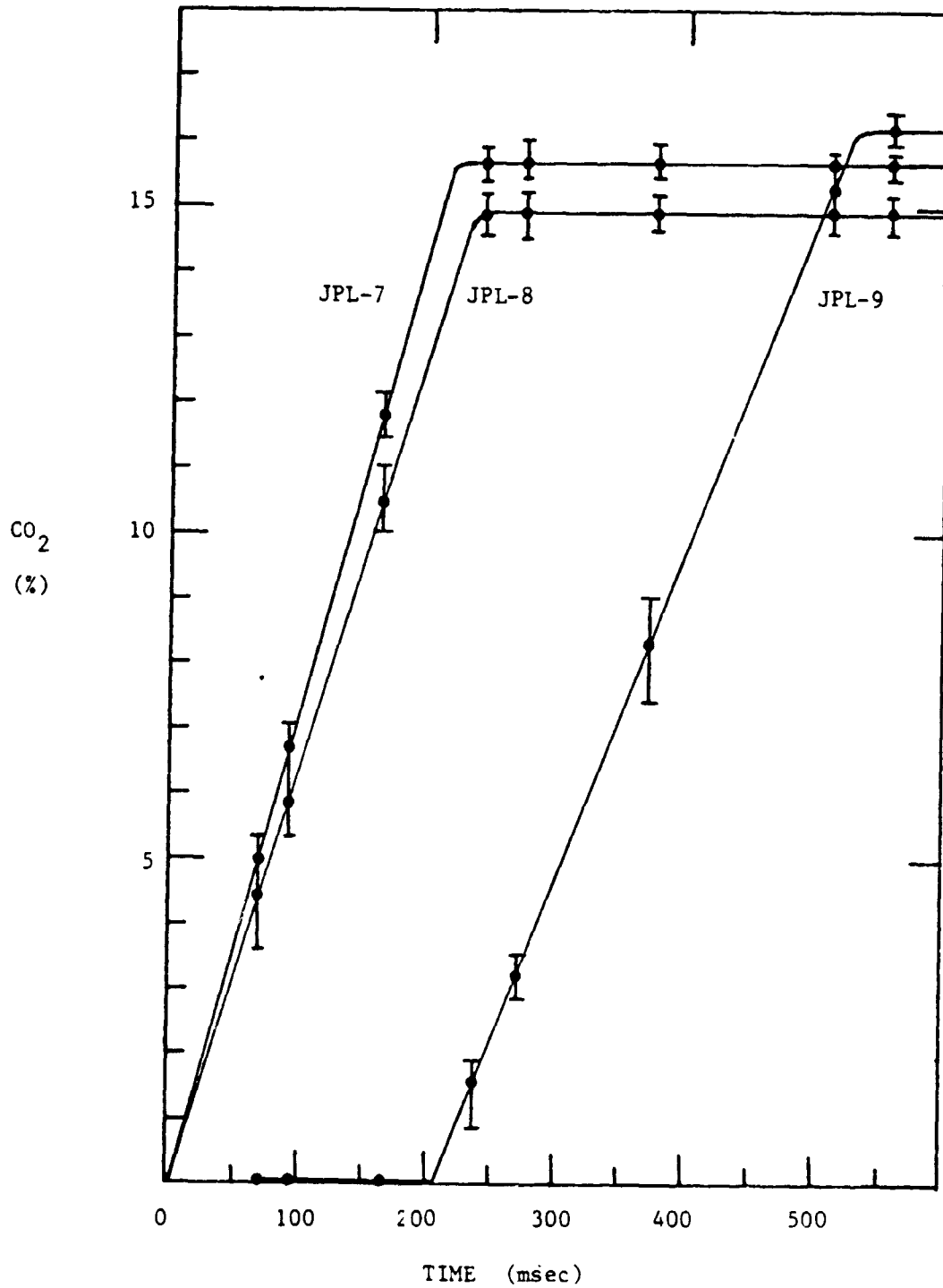


Figure 18. Gas-Phase Combustion Performance Characteristics of Raw and JPL-Desulfurized PSOC-230 Coal: JPL-7, JPL-8, JPL-9

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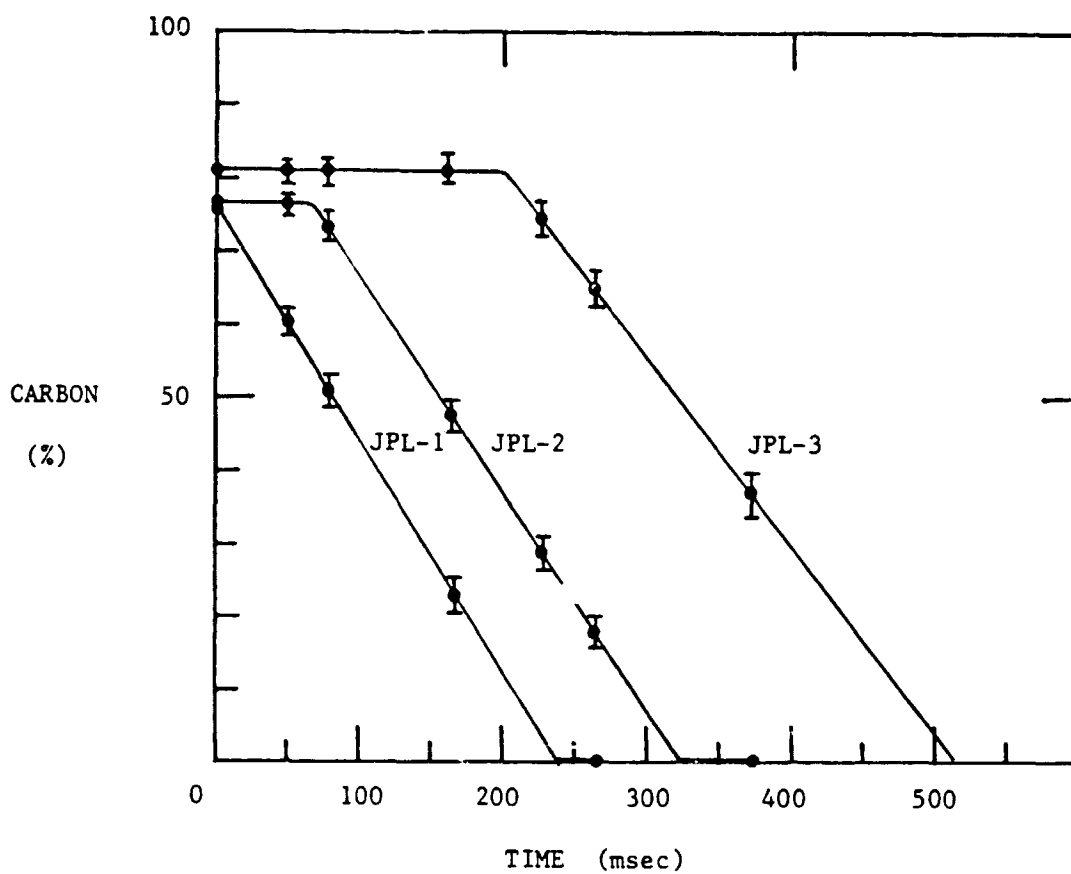


Figure 19. Solid-Phase Combustion Performance Characteristics of Raw and JPL-Desulfurized PSOC-282 Coal: JPL-1, JPL-2, JPL-3

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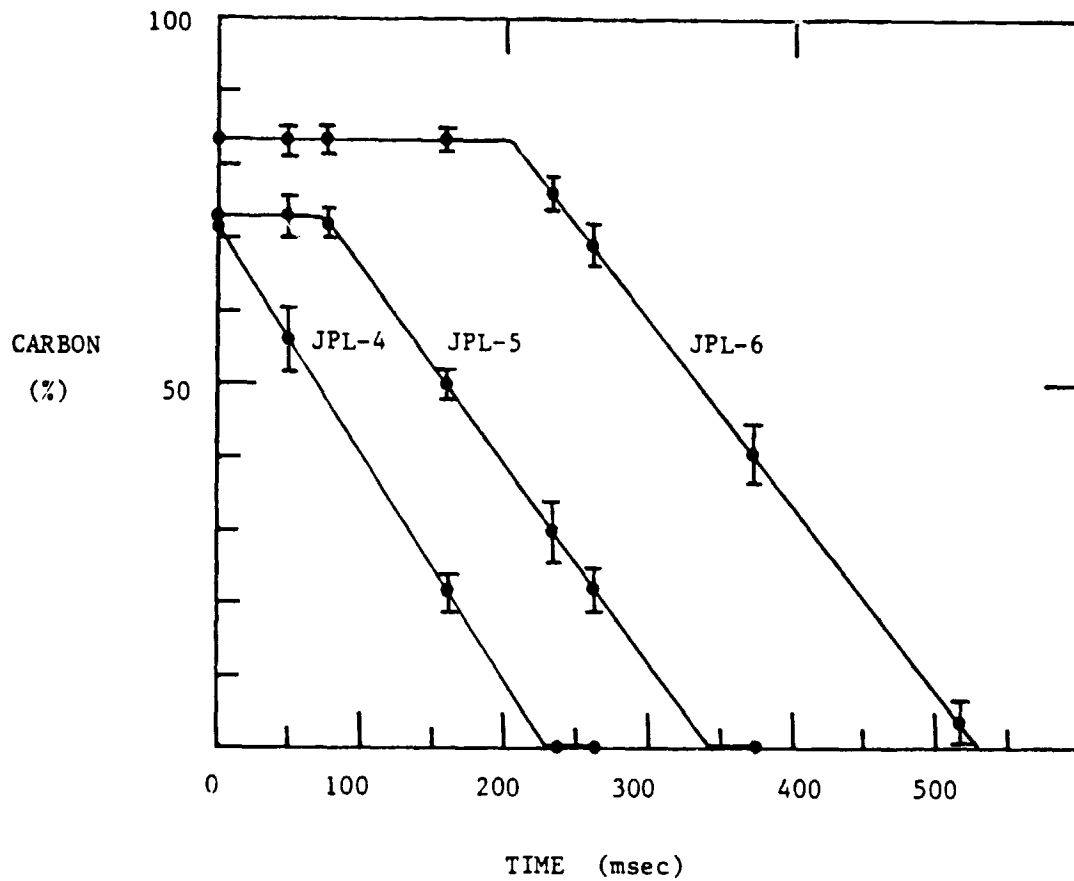


Figure 20. Solid-Phase Combustion Performance Characteristics of Raw and JPL-Desulfurized PSOC-276 Coal: JPL-4, JPL-5, JPL-6

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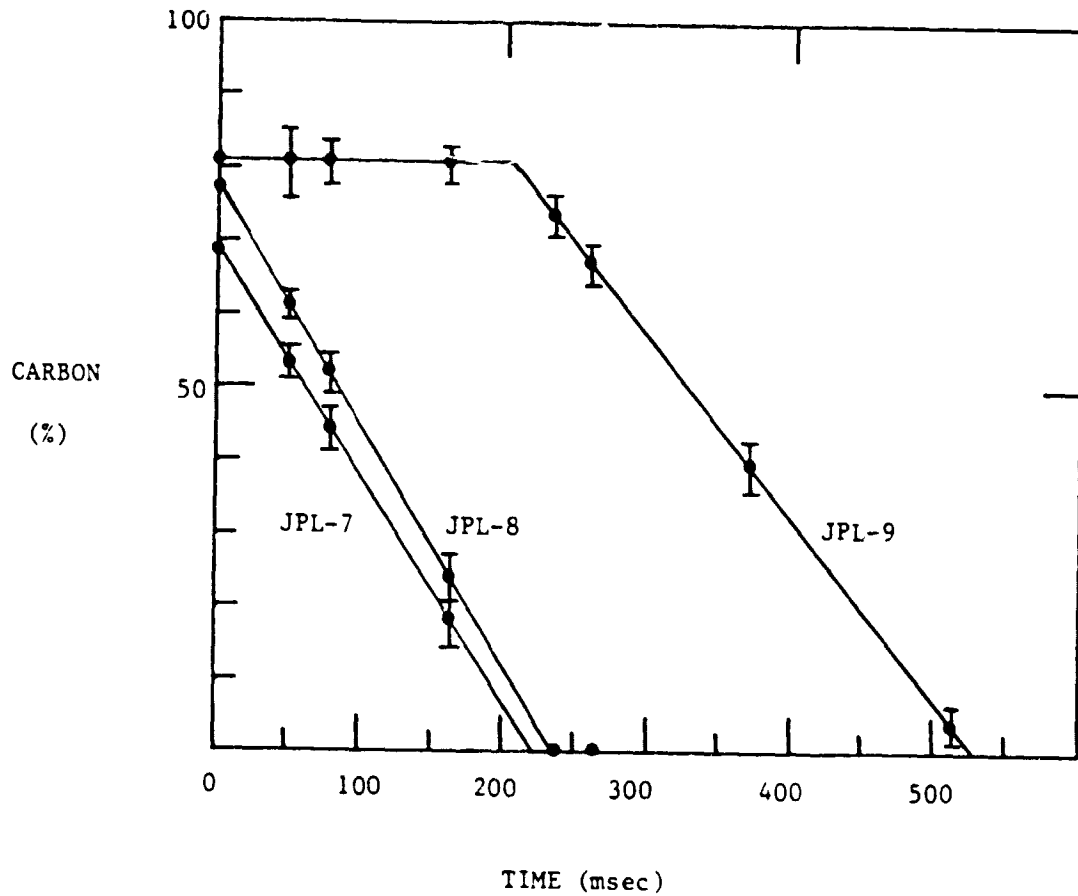


Figure 21. Solid-Phase Combustion Performance Characteristics of Raw and JPL-Desulfurized PSOC-230 Coal: JPL-7, JPL-8, JPL-9

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

All the data presented graphically thus far in Figs. 13-21 were numerically evaluated with the use of an Apple II microprocessor system in which are encoded equations that allow the quantification of the ignition, reaction, and burnout combustibility criteria. This computer analysis produced the contract-required data, and more, which have been listed in Table II. The volatile matter contents of the nine JPL-test coals correlate well with their respective combustion performance characteristics, as expected; this is why the volatile matter content of each coal is listed in Table II. Also included in Table II, is the SO_2 pollutant emission potential for each JPL-test coal assuming 100% conversion of fuel-bound-sulfur to SO_2 . These data will be used in the discussion of tradeoffs between loss of combustibility and desulfurization upon JPL chlorinolysis/hydrodesulfurization.

These singular combustibility data as generated by the PSU-FCL plane flame furnace allows one to decouple the flame initiation, propagation, and termination events from each other in order to identify which is primarily responsible for the loss of combustibility upon JPL-coal processing. Table II quantifies the following generic behavior in terms of fuel combustibility: as the volatile matter content decreases upon JPL-desulfurization, the respective raw coal's ignition time is delayed by a factor of 70, its burning velocity or overall reaction rate is retarded by a factor of 1.5, and its burnout time is prolonged by a factor of 1.4. These data clearly indicate that of the three events, ignition, reaction, and burnout, whose total represents the total flame residence time, ignition dominates. On average, for the 3 parent coals listed, decreasing the raw coal volatile matter content by 80% (from 36.6 to 6.8%) via JPL-chlorinolysis/hydrodesulfurization, results in a generic two-fold-plus increase (230 to 530 msec) in total flame residence time. Of the average 300 msec generic increase in the total flame residence time as the raw coal is generically desulfurized and devolatilized by about 75% and 80%, respectively, approximately 68% is directly attributable to the loss of ignition quality, i.e., a rather long ignition delay time (on average, ca. 200 msec) develops when there was none for the raw coal.

The remainder of the increase in total flame residence time upon severe JPL-desulfurization (ca. 100 msec) is attributable to the retardation of the raw coals overall reaction rate once ignited, as is reflected in the burning velocity data and is quantified in the burnout time data. On average, for the concomitant severe desulfurization and devolatilization of the raw coal, the burnout time increases from 230 to 324 msec. the retardation of raw coal burning velocities and lengthening of burnout times is probably the consequence of coal pore structural changes and fixed-carbon increases occurring upon JPL chlorination/hydrodesulfurization.

Before discussing recommendations for alleviating the aforementioned ignition and burnout problems, that seemingly will unavoidably occur upon JPL-coal desulfurization, one JPL test coal, JPL-8, must be singled-out for comment. The raw test coal (PSUC-230) of this series of fuels (see Table II), ignites without an ignition delay and burns out without difficulty. It cannot be directly fired in a coal combustor without the employment of SO_2 emission

Table 2. Combustibility Data on Raw and JPL-Desulfurized Coals

| PSU-FCL- Test No. | Coal | JPL Process | Volatile Matter (%) | Ignition Time (msec) | Ignition Delay Time (msec) | Burning Velocity (cm/sec) | Flame Length (cm) | Burnout Time (msec) | Total Flame Residence Time (msec) | SO ₂ Pollution (lb/10 ⁶ Btu) |
|-------------------------|----------|----------------|---------------------------|----------------------------|-------------------------------------|---------------------------------|-------------------------|---------------------------|---|--|
| JPL-1 | PSOC-282 | RAW | 33.8 | 0 | 3 | 31.3 | 40.3 | 239 | 239 | 2.44 |
| JPL-2 | PSOC-282 | CL | 25.10 | 61 | 64 | 28.1 | 44.8 | 266 | 327 | 1.04 |
| JPL-3 | PSOC-282 | CL/HDS | 7.57 | 198 | 201 | 23.2 | 54.3 | 322 | 520 | 0.49 |
| JPL-4 | PSOC-276 | RAW | 37.20 | 0 | 3 | 32.8 | 38.4 | 228 | 228 | 6.13 |
| JPL-5 | PSOC-276 | CL | 23.50 | 73 | 76 | 27.5 | 45.8 | 272 | 345 | 2.04 |
| JPL-6 | PSOC-276 | CL/HDS | 6.50 | 206 | 210 | 23.0 | 54.8 | 325 | 531 | 0.79 |
| JPL-7 | PSOC-230 | RAW | 38.90 | 0 | 2 | 33.7 | 37.4 | 222 | 222 | 1.46 |
| JPL-8 | PSOC-230 | CL | 34.20 | 0 | 3 | 31.6 | 39.9 | 237 | 237 | 1.03 |
| JPL-9 | PSOC-230 | CL/HDS | 6.25 | 208 | 212 | 22.9 | 54.9 | 326 | 534 | 0.61 |

control technology because it does not meet the Environmental Protection Agency (EPA) upper SO_2 emission limit of 1.2 pounds per million Btu fired (see right-most column of Table II). Upon mild JPL-desulfurization via chlorinolysis, JPL-8 becomes an SO_2 compliance coal. More important is the fact that this sulfur cleanup is accomplished with only a minimum alteration of PSOC-230 combustibility, i.e., it did not result in the appearance of an ignition delay time and it only causes a 7% increase in burnout time. Hence, JPL-chlorinated PSOC-230 could indeed be thought of as a premium fuel.

With this SO_2 -removal/loss of ignition-theme in mind, it is informative to ask the following question: what would the loss-of-ignition penalty from the loss-of-volatile matter content be for the other two raw coals, PSOC-282 and PSOC-276, for them to come into SO_2 -compliance as the direct result of JPL chlorinolysis or chlorinolysis plus hydrodesulfurization? Figure 22 has been prepared to help answer this question. In Figure 22, PSU-FCL-measured ignition delay time data and calculated maximum SO_2 emission data are plotted as a function of volatile matter content for all three types of raw coals. Also drawn in Figure 22 is the EPA upper emission limit for SO_2 . As should be obvious, the ignition delay time correlates linearly very well (95% coefficient) with volatile matter. A best straight line has thus been drawn through the ignition delay time data as a function of volatile matter content. Smooth curves have been drawn through the SO_2 emission data as a function of volatile matter to find the point at which they intersect the EPA SO_2 upper emission limit. As already discussed, mildly desulfurized PSOC-230 raw coal complies with the SO_2 limit and is readily ignitable, the latter because its volatile matter content remains high. For PSOC-282 raw coal, compliance desulfurization via the JPL process would require the reduction of its volatile matter content to about 26.8% (from 33.8%). This loss-of-volatile matter content upon SO_2 compliance would result in an ignition delay penalty of only 50 msec. For PSOC-276 coal to become an SO_2 compliance coal via JPL treatment, it would have its volatile matter content reduced drastically, from 37.2% to 16%. This would result in an ignition time delay penalty of about 130 msec.

How can these results be best interpreted? From his decade of experience in combustion research, Prof. Reutner is aware of an industrial "rule of thumb" that states that utilities typically think coals having a volatile matter content of 20% or greater will offer no combustibility problems, whereas those having less than 20% may very well be troublesome. The last determination in this report on the loss of volatile matter content-loss of ignition tradeoff upon JPL-desulfurization produces a very encouraging result, from JPL's viewpoint: the JPL-chlorinolysis and/or hydrodesulfurization process is a promising means for producing SO_2 -compliance coals from high-sulfur PSOC-282 and 276 coal feedstocks that will either surpass or nearly-miss the coal combustion industries cutoff limit for acceptable combustibility.

In summary, the latter analysis of the plane flame combustibility data on JPL-desulfurized coals seems to indicate that in two cases out of three (PSOC-282 and 230), the JPL desulfurization process produces a coal that is both clean (in terms of SO_2 pollution) and easy (in terms of ignitibility) to burn.

The discussion thus far has primarily focused on stopping the JPL desulfurization process at the SO_2 compliance limit. One must ask if one would even contemplate using the severely JPL-processed coals, given their somewhat

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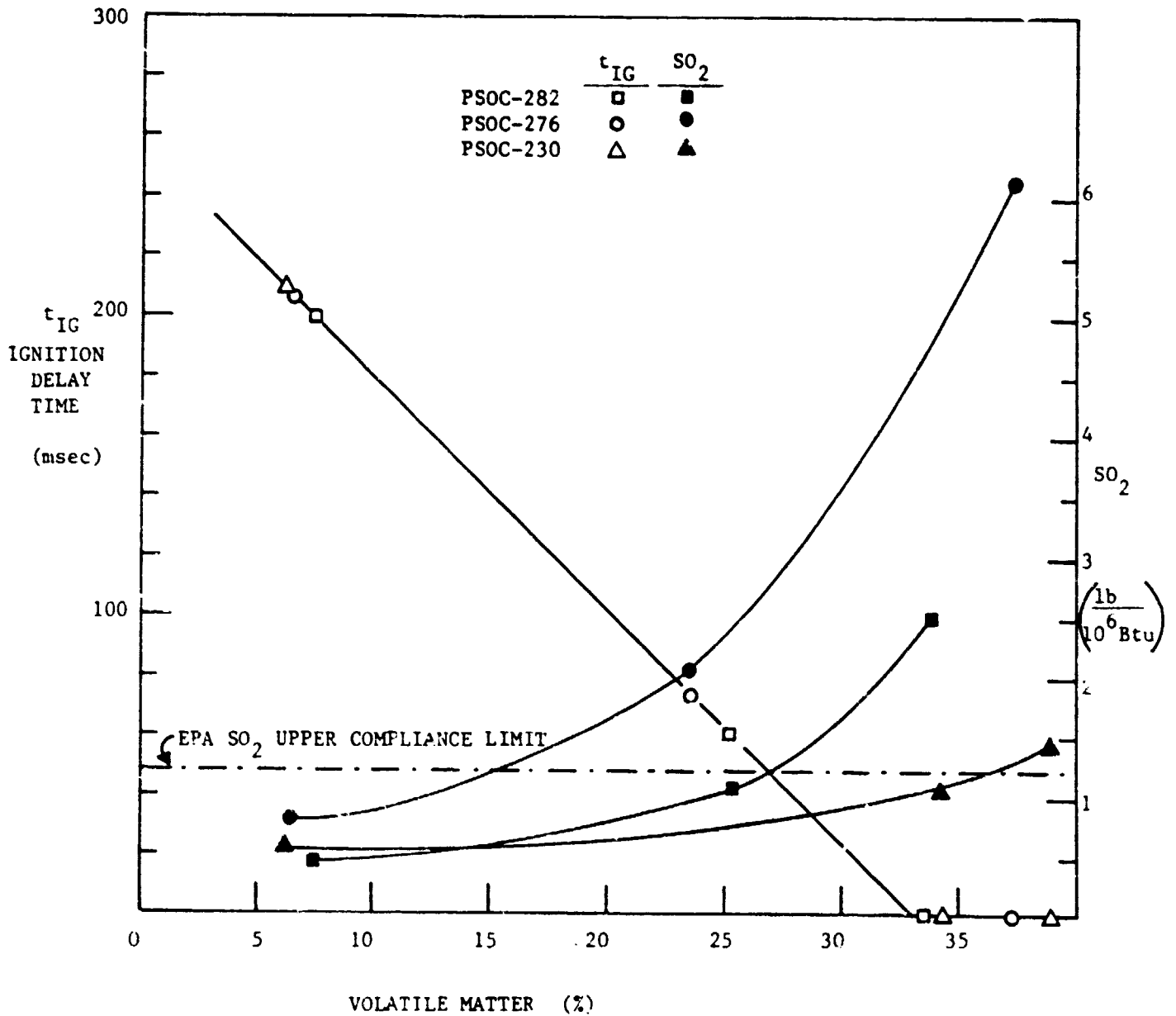


Figure 22. Trade-Off Between Sulfur Removal and Ignition Performance upon JPL-Desulfurization as a Function of Coal Volatile Matter Content

inferior combustibility characteristics. This question actually reduces to one that asks if these severely desulfurized, very low volatile JPL-process coals could be burned in a utility boiler. The Principal Investigator's answer to this question is an rather optimistic yes, and so for two reasons. The first has to do with the fact that the low-sulfur, low-volatile, severely JPL-processed coals need not be directly burned neatly. In other words, the very-low sulfur JPL-processed coals could be blended with higher-sulfur coals to produce a coal that simultaneously meets the utility industry's combustibility criteria and EPA's SO₂ pollution limit. Gogot and Hensel of Combustion Engineering, a major utility boiler manufacturer, have carefully considered the concept of blending coals to meet SO₂ emission standards [3]. Prof. Reuther suggests that if an easy, but dirty to burn raw (high volatile, high sulfur) coal were blended with a difficult, but clean to burn (low volatile, low-sulfur) JPL-desulfurized coal, the coal-fired utility boiler industry would have a premium, easy and clean to burn coal and the JPL would have a promising market for its chlorinolysis/hydrodesulfurization process.

Secondly, Prof. Reuther has asked the question of whether or not burner technology exists to help to circumvent the ignition delay problem for the severely desulfurized coals. One finds the answer to this question in the combustion research literature that concerns directly-firing pulverized anthracite coal, a natural low-sulfur, low-volatile solid fuel [4-6]. The universal finding of these programs indicated that long ignition delay times could be shortened by enhancing recirculation of hot combustion gases near the pulverized anthracite burner [3, 4] and that sluggish flame velocities could be accelerated by increasing the fineness of the pulverized fuel grind [3]. Moreover, judicious selection of flame-furnace configuration, especially, that involving vertical-firing, is another means by which to acceptably ignite and burnout low-volatile fuels (6), such as those with less than 15% volatile matter. Down-fired coal combustors could now, in principle, successfully fire low-volatile severely JPL-desulfurized coals. It would be useful to learn how many of these down-fired units are currently in operation.

In conclusion, the PSU-FCL plane flame furnace combustion tests on JPL-desulfurized coals indicate that although the combustibility characteristics of high-volatile/high sulfur coals are diminished upon JPL desulfurization, their average extent is one that should not be thought of as prohibiting JPL-process coal from direct use in utility boilers. It is the expert opinion of the Principal Investigator that the JPL desulfurization process appears to offer promise and competitiveness with other SO₂ control strategies, such as flue gas desulfurization, fluidized bed combustion, coal conversion, and mechanical beneficiation [7], and research and development concerning it should be actively continued.

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